Submillimeter Spectroscopy of the Major Isotopes of Water[1]

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Extensive new measurements in the region 300–1100 GHz for the major isotopes of water in both the ground and first excited vibrational states are reported. These results are used as the basis for centrifugal distortion analyses of these species that are based solely upon microwave data. Comparisons are made with both earlier microwave work and with previous analyses based upon weighted data sets of microwave and high-resolution infrared data. The new measurements reported in this paper represent more than a third of the total microwave data currently available.

I. INTRODUCTION

In addition to being one of the most pervasive, water is one of the most fundamentally important molecular species, both to spectroscopists and to workers in many other fields. It is the prototype bent, triatomic rotor and, as such, has served for a number of years as a major testing ground for centrifugal distortion theories. Its abundance and absorptivity are large enough so that even its rarer isotopic species play a role in atmospheric transmission and are detectable in the interstellar medium. Thus, the spectral properties of water are significant to the atmospheric, communications, astronomical, and radar communities.

Because of the small moments of inertia and large rotational constants of the several isotopes of water, the microwave spectra of these species are very sparse. In the limiting case of H_2O, only two transitions fall below 300 GHz. Only by means of millimeter and submillimeter techniques has it been possible to acquire enough data for meaningful microwave analyses of these and other light asymmetric rotors (*1–6*).

Infrared spectroscopists have carried out a large number of studies of water and its isotopes. These include the early studies of Mecke *et al.* (*7*) and Randall *et al.* (*8*); the extensive work of Benedict (*9*) and his co-workers; and the recent work of Camy-Peyret *et al.* (*10, 11*), Kauppinen *et al.* (*12*), Toth *et al.* (*13*), and Partridge (*14*). This work has produced a wealth of data of ever increasing accuracy. In centrifugal distortion analyses of these infrared data, microwave data is usually used to determine that portion of the ground vibrational state rotational structure with which it is strongly correlated.

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In this paper, we report extensive new millimeter and submillimeter microwave measurements of H_2O, HDO, and D_2O in both the ground and first excited vibrational state. These measurements are largely in the region 300–1100 GHz, and have been made with the experimental techniques we have developed for this spectral region (15). We also report the results of centrifugal distortion analyses based upon our newly extended data sets.

II. EXPERIMENTAL DETAILS

The work described in this paper requires a high-resolution microwave spectrometer capable of working in the spectral region between 300 and 1100 GHz. The evolution of our system has been described in a series of papers, and the experimental details are contained therein (15–17). Briefly, a phase-locked 55-GHz klystron, referenced to WWVB, is used to drive a crystal harmonic generator. Harmonics as high as the 19th are radiated via quasioptical techniques through a 1-m-long, 1-cm-radius copper cell. The submillimeter power was detected by a 1.5-K InSb detector.

III. THEORY

Watson's (18) introduction of his reduced centrifugal distortion Hamiltonian removed the fitting indeterminacy previously associated with asymmetric rotors and made possible accurate analyses of the isotopes of water. Watson's Hamiltonian is in the form of a power series that is easily extended to arbitrarily high order. This Hamiltonian, through terms in 8th power, is given by

$$\mathscr{H} = \mathscr{H}_r + \mathscr{H}_d^{(4)} + \mathscr{H}_d^{(6)} + \mathscr{H}_d^{(8)}. \tag{1}$$

$$\mathscr{H}_r = \frac{1}{2}(B + C)P^2 + \left[A - \frac{1}{2}(B + C) \right](P_z^2 - b_p P_-^2), \tag{2}$$

$$\mathscr{H}_d^{(4)} = -\Delta_J P^4 - \Delta_{JK} P^2 P_z^2 - \Delta_K P_z^4 - 2\delta_J P^2 P_-^2 - \delta_K(P_z^2 P_-^2 + P_-^2 P_z^2), \tag{3}$$

$$\mathscr{H}_d^{(6)} = H_J P^6 + H_{JK} P^4 P_z^2 + H_{KJ} P^2 P_z^4 + H_K P_z^6 + 2h_J P^4 P_-^2$$

$$\quad + h_{JK} P^2(P_z^2 P_-^2 + P_-^2 P_z^2) + h_K(P_z^4 P_-^2 + P_-^2 P_z^4), \tag{4}$$

$$\mathscr{H}_d^{(8)} = L_J P^8 + L_{JJK} P^6 P_z^2 + L_{JK} P^4 P_z^4 + L_{KKJ} P^2 P_z^6 + L_K P_z^8 + 2l_J P^6 P_-^2$$

$$\quad + l_{JK} P^4(P_z^2 P_-^2 + P_-^2 P_z^2) + l_{KJ} P^2(P_z^4 P_-^2 + P_-^2 P_z^4) + l_K(P_z^6 P_-^2 + P_-^2 P_z^6), \tag{5}$$

where Δ_J, etc. are the quartic distortion coefficients; H_J, etc. are the sextic distortion coefficients; L_J, etc. are the determinable 8th order distortion coefficients; $b_p = (C - B)/(2A - B - C)$ is Wang's asymmetry parameter, $P^2 = P_x^2 + P_y^2 + P_z^2$; and where we have defined

$$P_-^2 = P_x^2 - P_y^2. \tag{6}$$

We have previously discussed the application of this theory to microwave data sets in series of papers on the isotopes of water and hydrogen sulfide (1–5). Steenbeckliers and Bellet have discussed its application to D_2O (6). Benedict et al. (19) have used the theory of Kneizys et al. (20) in an analysis of D_2O. Watson's theory (suitably modified for resonating states) has been used by Flaud and Camy-Peyret in a series

of papers with several coauthors for the analysis of the excellent infrared data of Guelachvili (10, 21–25).

Although the form of the centrifugal distortion theory discussed above is well established, care must be exercised both in its application to molecules like water, and in the interpretation of the results of these analyses. This is especially true if it is a weighted fit of microwave and infrared data. Most of the potential problems are related to the fact that the microwave measurements are more accurate, but less global, than the infrared data. In a recent and fairly typical example on D_2O, Papineau et al. (24) fit 36 microwave lines and 228 infrared energy levels with rms deviations of 0.127 MHz ($\sim$0.000004 cm^{-1}) and 0.0011 cm^{-1} (33 MHz), respectively. In a similar study on HDO, Papineau et al. (25) fit 56 microwave lines and 188 infrared energy levels with rms deviations of 2.26 MHz ($\sim$0.0001 cm^{-1}) and 0.003 cm^{-1} (90 MHz), respectively. For both HDO and D_2O, the accuracy of the microwave data set is about the same. Clearly, in these mixed fits choices must be made about the relative weights of the microwave and infrared data and the number of terms to be retained in the Hamiltonian. If the microwave lines are to be fitted to their experimental uncertainty they must be weighted accordingly, and the model must contain enough terms to be accurate at the level of the microwave data. If one desires that the analysis predicts observed microwave transitions, as well as transitions with similar quantum numbers with maximum accuracy, then heavy microwave weighting and large Hamiltonians are required. On the other hand, if one desires to extrapolate the results of the analyses to predict transitions and energy levels far removed from those observed, the number of high-order constants should be minimized and the weights on the microwave lines adjusted accordingly. For analyses of pure microwave data sets, the same rules apply except that weighting is no longer an issue. It should be expected that analyses of pure microwave data that are optimized (by the inclusion of high-order terms) to calculate rotational constants, and to predict the millimeter and submillimeter rotational spectrum, will not extrapolate well to calculate unobserved energy levels.

IV. RESULTS

A. Ground State of HDO

We have previously reported an analysis of the ground vibrational state of HDO that was based upon 53 microwave lines (2). For that analysis, we measured 33 transitions at frequencies as high as 750 GHz. These were combined with the previously available lower frequency data set (26–44) to form the basis for a centrifugal distortion analysis.

In this work, we report an additional 26 transitions, mostly in the region 500–1100 GHz, and a detailed analysis. This new analysis substantially extends the range, both in frequency and quantum number, over which the rotational spectrum of HDO can be accurately calculated. These new microwave results also substantially increase the range over which the microwave data makes very strong contributions to the calculation of the ground state energy level structure in mixed analyses with infrared data. The microwave data set is shown in Table I. Those transitions marked with a

TABLE I

Observed Microwave Transitions for HDO (MHz)

TRANSITION	OBSERVED	CALCULATED [a]	O.-C.	STR. [b]	ENERGY [c]	REF. [d]
5(4, 1)- 5(4, 2)	486.53	486.54(0.00)	-0.01	5.8347	480.2424	31,33
3(3, 0)- 3(3, 1)	824.67	824.67(0.00)	0.00	5.2379	233.0236	28,31,33
6(4, 2)- 6(4, 3)	2394.56	2394.59(0.01)	-0.03	4.8903	573.8906	28,31
9(5, 4)- 9(5, 5)	3044.71	3044.78(0.02)	-0.07	5.1523	1082.7861	28,31
4(3, 1)- 4(3, 2)	5702.78	5702.84(0.01)	-0.06	4.0105	295.4871	43,30
7(4, 3)- 7(4, 4)	8577.81	8577.89(0.02)	-0.08	4.1828	683.3239	30,37
10(5, 5)-10(5, 6)	8837.21	8837.22(0.04)	-0.01	4.5969	1238.7964	30,40
2(2, 0)- 2(2, 1)	10278.25	10278.23(0.00)	0.01	3.3152	108.9262	27,34-36
6(2, 4)- 7(0, 7)	11618.20	11617.92(0.07)	0.28	0.0216	403.1613	40
3(2, 1)- 4(1, 4)	20460.01	20460.00(0.05)	0.01	0.2230	156.3822	27,39
5(3, 2)- 5(3, 3)	22307.67	22307.53(0.02)	0.14	3.2184	373.6657	44,26,27
11(5, 6)-11(5, 7)	22581.57	22581.54(0.06)	0.03	4.1175	1410.5700	30,40
8(4, 4)- 8(4, 5)	24884.77	24884.92(0.03)	-0.15	3.6202	808.5633	29,30
7(1, 7)- 6(2, 4)	26880.38	26880.28(0.06)	0.10	0.1485	403.5489	29,30
11(7, 5)-12(6, 6)	28668.34	28668.44(0.09)	-0.10	0.6631	1756.3924	42
11(7, 4)-12(6, 7)	31670.43	31670.32(0.09)	0.11	0.6631	1756.2932	42
13(2,12)-12(3, 9)	45902.54	45902.54(0.11)	-0.00	0.1747	1405.1301	42
3(2, 1)- 3(2, 2)	50236.30	50236.30(0.02)	-0.00	2.2739	155.3890	27,32
12(5, 7)-12(5, 8)	51917.87	51917.91(0.11)	-0.04	3.6902	1598.0731	38,40
4(3, 1)- 5(2, 4)	61185.95	61185.95(0.05)	0.00	0.2981	293.6364	43,38
9(4, 5)- 9(4, 6)	61704.59	61704.71(0.05)	-0.12	3.1484	949.5779	43,38
6(3, 3)- 6(3, 4)	64427.34	64427.36(0.04)	-0.02	2.6433	467.5144	43,38
6(0, 6)- 5(2, 3)	69550.58	69550.66(0.05)	-0.08	0.0266	303.9947	39
1(1, 0)- 1(1, 1)	80578.15	80578.24(0.02)	-0.09	1.5000	29.8086	32
7(3, 5)- 6(4, 2)	87962.81	87962.72(0.06)	0.09	0.4478	573.9704	2
5(1, 5)- 4(2, 2)	120778.19	120778.15(0.05)	0.04	0.2378	221.8360	32,2
10(4, 6)-10(4, 7)	134770.22	134770.21(0.08)	0.01	2.7338	1106.2654	38,2
6(1, 6)- 5(2, 3)	138530.57	138530.41(0.05)	0.16	0.2001	303.9947	32,2
4(2, 2)- 4(2, 3)	143727.21	143727.25(0.03)	-0.04	1.6844	217.0418	32,2
7(3, 4)- 7(3, 5)	151616.19	151616.17(0.05)	0.02	2.1883	576.9046	38,2
9(6, 4)-10(5, 5)	160329.46	160329.46(0.08)	-0.01	0.5330	1239.0912	39,2
9(6, 3)-10(5, 6)	169246.05	169246.04(0.08)	0.01	0.5327	1238.7964	2
3(2, 1)- 4(0, 4)	207110.65	207110.75(0.07)	-0.10	0.0178	150.1562	41
7(2, 5)- 8(1, 8)	207345.71	207345.79(0.07)	-0.08	0.1053	513.2070	38,2
9(4, 6)- 8(5, 3)	210310.65	210310.61(0.08)	0.04	0.5867	942.5627	38,2
3(1, 2)- 2(2, 1)	225896.72	225896.65(0.05)	0.07	0.2281	108.9262	38,2
2(1, 1)- 2(1, 2)	241561.55	241561.49(0.04)	0.06	0.8333	58.1269	32,2
7(3, 4)- 6(4, 3)	241973.57	241973.49(0.06)	0.08	0.4596	573.8906	38,2
5(2, 3)- 4(3, 2)	255050.26	255050.30(0.06)	-0.04	0.3376	295.4871	2
7(5, 3)- 8(4, 4)	258223.76	258223.77(0.08)	-0.01	0.4016	809.3933	2
2(2, 0)- 3(1, 3)	266161.07	266161.04(0.05)	0.03	0.1323	100.3909	38,2
9(4, 5)- 8(5, 4)	272907.54	272907.62(0.07)	-0.08	0.5900	942.5329	2
7(5, 2)- 8(4, 5)	283318.59	283318.60(0.07)	-0.01	0.4008	808.5633	2
8(3, 5)- 8(3, 6)	305038.55	305038.46(0.06)	0.09	1.8120	701.6203	2
5(2, 3)- 5(2, 4)	310533.29	310533.41(0.05)	-0.12	1.2959	293.6364	2
6(2, 5)- 5(3, 2)	313750.62	313750.63(0.06)	-0.01	0.4500	374.4098	2
5(4, 2)- 6(3, 3)	317151.25	317151.22(0.06)	0.03	0.2696	469.6634	2
11(5, 7)-10(6, 4)	332949.59	332949.54(0.09)	0.05	0.7205	1399.4640	*
3(3, 1)- 4(2, 2)	335395.50	335395.49(0.06)	0.01	0.1378	221.8360	2
11(5, 6)-10(6, 5)	355841.38	355841.40(0.09)	-0.02	0.7214	1399.4536	*
5(3, 2)- 6(1, 5)	356835.85	356835.91(0.11)	-0.06	0.0169	362.5070	*
5(4, 1)- 6(3, 4)	382065.10	382065.11(0.06)	-0.01	0.2670	467.5144	2
1(0, 1)- 0(0, 0)	464924.52	464924.51(0.03)	0.01	1.0000	0.0000	2
3(3, 0)- 4(2, 3)	479947.37	479947.41(0.06)	-0.04	0.1313	217.0418	2
3(1, 2)- 3(1, 3)	481779.50	481779.46(0.05)	0.04	0.5873	100.3909	2
2(0, 2)- 1(1, 1)	490596.64	490596.63(0.04)	0.01	0.6328	29.8086	2
1(1, 0)- 1(0, 1)	509292.42	509292.44(0.04)	-0.02	1.5000	15.5082	2
10(7, 4)-11(6, 5)	528958.35	528958.41(0.08)	-0.06	0.4846	1570.1011	*
10(7, 3)-11(6, 6)	529990.76	529990.72(0.08)	0.05	0.4846	1570.0669	*
8(3, 6)- 7(4, 3)	539935.90	539935.99(0.07)	-0.09	0.6287	683.6100	2
9(3, 6)- 9(3, 7)	540374.26	540374.31(0.11)	-0.05	1.5030	841.3678	*
8(2, 6)- 9(1, 9)	548555.01	548554.99(0.11)	0.02	0.0753	634.7909	*

* are the newly measured lines. Table II shows the constants calculated from the data, along with our earlier results. Two very nice analyses of the infrared spectrum of HDO have been published recently (*13, 25*). Both of these use a mixture of new

TABLE I—*Continued*

TRANSITION	OBSERVED	CALCULATED	O.-C.	STR.	ENERGY	REF.
6(2, 4)- 6(2, 5)	559816.74	559816.44(0.07)	0.30	1.0293	384.8754	2
2(1, 1)- 2(0, 2)	599926.71	599926.59(0.04)	0.12	2.2787	46.1731	2
7(2, 6)- 6(3, 3)	622482.57	622482.57(0.07)	0.00	0.5477	469.6634	*
8(6, 3)- 9(5, 4)	663044.56	663044.65(0.08)	-0.08	0.3574	1082.8877	*
8(6, 2)- 9(5, 5)	666105.69	666105.59(0.08)	0.11	0.3573	1082.7861	*
10(4, 7)- 9(5, 4)	700845.59	700845.72(0.09)	-0.13	0.7778	1082.8877	2
3(1, 2)- 3(0, 3)	753411.15	753410.95(0.04)	0.20	2.7523	91.3302	2
6(5, 2)- 7(4, 3)	766165.66	766165.66(0.07)	-0.01	0.2310	683.6100	*
6(5, 1)- 7(4, 4)	774779.02	774779.04(0.07)	-0.03	0.2308	683.3239	*
4(1, 3)- 4(1, 4)	797487.02	797487.09(0.06)	-0.08	0.4627	156.3822	*
4(1, 3)- 3(2, 2)	827263.39	827263.39(0.05)	-0.00	0.5798	155.3890	*
4(4, 1)- 5(3, 2)	836994.63	836994.57(0.08)	0.05	0.1084	374.4098	*
10(4, 6)- 9(5, 5)	838660.82	838660.71(0.09)	0.11	0.7889	1082.7861	*
8(2, 7)- 7(3, 4)	838953.29	838953.20(0.11)	0.09	0.5665	581.9619	*
2(1, 2)- 1(1, 1)	848961.84	848961.73(0.05)	0.11	1.5000	29.8086	*
8(3, 5)- 7(4, 4)	853552.36	853552.34(0.08)	0.02	0.6700	683.3239	*
1(1, 1)- 0(0, 0)	893638.67	893638.71(0.06)	-0.05	1.0000	0.0000	*
6(2, 4)- 5(3, 3)	895874.36	895874.60(0.07)	-0.24	0.5887	373.6657	*
2(0, 2)- 1(0, 1)	919310.88	919310.83(0.05)	0.05	1.9891	15.5082	*
4(1, 3)- 4(0, 4)	984137.83	984137.84(0.07)	-0.01	2.9023	150.1562	*
3(0, 3)- 2(1, 2)	995411.50	995411.45(0.05)	0.05	1.4240	58.1269	*
2(1, 1)- 1(1, 0)	1009944.70	1009944.98(0.04)	-0.28	1.5000	32.4964	*

[a] Uncertainty in calculated frequency as per discussion in reference 1.
[b] Line strength calculated as discussed in reference 45.
[c] Energy of lower state in reciprocal cm.
[d] * this work. Otherwise, the observed frequency was taken from the last reference listed.

TABLE II

Spectral Constants of HDO (MHz)

Constant	This Work value 2σ	De Lucia et al.[a] value 2σ	Papineau et al.[b] value 2σ	Toth et al.[c] value 2σ
A	701931.633 0.138	701931.50 0.22	701931.71 1.05	701929.32 2.40
B	272912.747 0.071	272912.60 0.11	272911.84 0.51	272910.76 1.02
C	192055.118 0.061	192055.25 0.10	192055.46 0.08	192055.89 0.87
Δ_J	10.84139 0.0024	10.8375 0.0058	10.8346 0.0060	10.8094 0.0025
Δ_{JK}	34.26160 0.0162	34.208 0.036	34.090 0.048	34.272 0.021
Δ_K	377.07590 0.020	377.078 0.026	377.373 0.048	375.868 0.46
δ_J	3.6496679 0.0006	3.6471 0.0014	3.6436 0.0022	3.6404 0.0027
δ_K	63.17292 0.030	63.087 0.035	62.958 0.051	62.399 0.078
H_J	$(0.125995\ 0.0028)\times10^{-2}$	$(0.1128\ 0.0099)\times10^{-2}$	$(0.1198\ 0.0026)\times10^{-2}$	$(0.1053\ 0.0011)\times10^{-2}$
H_{JK}	$(0.769419\ 0.0058)\times10^{-1}$	$(0.7344\ 0.0092)\times10^{-1}$	$(0.7208\ 0.0063)\times10^{-1}$	$(0.7198\ 0.0012)\times10^{-1}$
H_{KJ}	-0.2737588 0.0010	-0.2740 0.0022	-0.2779 0.0012	-0.26088 0.00045
H_K	1.4678465 0.0018	1.4651 0.0027	1.4846 0.0018	1.36672 0.00072
h_J	$(0.625943\ 0.0060)\times10^{-3}$	$(0.6546\ 0.0150)\times10^{-3}$	$(0.6251\ 0.0099)\times10^{-3}$	$(0.6332\ 0.012)\times10^{-3}$
h_{JK}	$(0.362563\ 0.0030)\times10^{-1}$	$(0.3096\ 0.0037)\times10^{-1}$	$(0.3047\ 0.0063)\times10^{-1}$	$(0.3001\ 0.0036)\times10^{-1}$
h_K	0.5563727 0.0052	0.5549 0.0053	0.5506 0.0014	0.4443 0.0183
L_J	$(-0.680456\ 0.073)\times10^{-4}$	$(0.219\ 0.040)\times10^{-5}$	$(-0.3186\ 0.0225)\times10^{-4}$	$(0.327\ 0.051)\times10^{-6}$
L_{JJK}	$(-0.840185\ 0.042)\times10^{-3}$	$(-0.746\ 0.046)\times10^{-3}$	$(-0.7221\ 0.0081)\times10^{-3}$	
L_{JK}	$(0.2821874\ 0.0118)\times10^{-2}$	$(0.2866\ 0.0091)\times10^{-2}$	$(0.2587\ 0.0015)\times10^{-2}$	
L_{KKJ}	$(-0.7796532\ 0.0104)\times10^{-2}$	$(-0.7557\ 0.0101)\times10^{-2}$	$(-0.7534\ 0.0017)\times10^{-2}$	$(-0.31628\ 0.00090)\times10^{-2}$
ℓ_J	$(-0.239323\ 0.0110)\times10^{-3}$		$(-0.21062\ 0.02129)\times10^{-4}$	
ℓ_{JK}	$(-0.504700\ 0.052)\times10^{-2}$			
ℓ_K	$(-0.503495\ 0.0188)\times10^{-2}$	$(-0.569\ 0.022)\times10^{-2}$	$(-0.57310\ 0.00135)\times10^{-2}$	
P_{JK}	$(0.253525\ 0.048)\times10^{-5}$			
P_{KJ}	$(-0.748519\ 0.146)\times10^{-5}$			
P_{KKJ}	$(0.685976\ 0.180)\times10^{-5}$			
P_K	$(0.276900\ 0.0196)\times10^{-4}$		$(0.97\ 0.19)\times10^{-6}$	
p_{KKJ}	$(0.110488\ 0.0172)\times10^{-4}$		$(0.1749\ 0.0014)\times10^{-4}$	
p_K			$(0.140\ 0.002)\times10^{-4}$	
T_K	$(-0.106392\ 0.0132)\times10^{-6}$			
rms MW	0.112	0.116	2.26	------[d]
rms IR	--	--	90	201[d]

[a] Reference 2.
[b] Reference 25.
[c] Reference 13.
[d] rms deviation of energy levels.

TABLE III

Energy Levels of HDO (cm⁻¹)

LEVEL			THIS WORK	TOTH et al.[a]	PAPINEAU et al.[b]
0	0	0	0.000000	0.00000	0.0000
1	0	1	15.508212	15.50821	15.5082
1	1	1	29.808579	29.80858	29.8086
1	1	0	32.496380	32.49638	32.4964
2	0	2	46.173121	46.17312	46.1731
2	1	2	58.126894	58.12689	58.1269
2	1	1	66.184518	66.18452	66.1845
2	2	1	108.926229	108.9260	108.9261
2	2	0	109.269074	109.2690	109.2690
3	0	3	91.330246	91.3303	91.3301
3	1	3	100.390898	100.3908	100.3908
3	1	2	116.461331	116.4612	116.4612
3	2	2	155.388991	155.3890	155.3891
3	2	1	157.064693	157.0647	157.0648
3	3	1	233.023655	233.0239	233.0236
3	3	0	233.051163	233.0514	233.0511
4	0	4	150.156222	150.1566	150.1560
4	1	4	156.382221	156.3822	156.3823
4	1	3	182.983527	182.9831	182.9834
4	2	3	217.041841	217.0418	217.0418
4	2	2	221.836066	221.8359	221.8360
4	3	2	295.487157	295.4874	295.4871
4	3	1	295.677383	295.6772	295.6773
4	4	1	402.328993	402.3291	402.3281
4	4	0	402.330815	402.3310	402.3308
5	0	5	221.946036	221.9463	221.9459
5	1	5	225.864791	225.8647	225.8647
5	1	4	265.236156	265.2361	265.2359
5	2	4	293.636439	293.6366	293.6363
5	2	3	303.994719	303.9945	303.9946
5	3	3	373.665760	373.6660	373.6657
5	3	2	374.409860	374.4100	374.4098
5	4	2	480.242515	480.2428	480.2421
5	4	1	480.258744	480.2591	480.2583
5	5	1	615.968601	615.9687	615.9686
5	5	0	615.968709	615.9687	615.9686
6	0	6	306.314679	306.3146	306.3145
6	1	6	308.615596	308.6155	308.6155
6	1	5	362.507095	362.5071	362.5069
6	2	5	384.875454	384.8754	384.8753
6	2	4	403.548921	403.5488	403.5488
6	3	4	467.514424	467.5143	467.5140
6	3	3	469.663489	469.6636	469.6631
6	4	3	573.890636	573.8908	573.8903
6	4	2	573.970511	573.9705	573.9702
6	5	2	709.166625	709.1663	709.1663
6	5	1	709.167809	709.1675	709.1677
6	6	1	872.790411	872.7896	872.7882
6	6	0	872.790417	872.7896	872.7882
7	0	7	403.161389	403.1613	403.1614
7	1	7	404.445550	404.4456	404.4454
7	1	6	473.917576	473.9176	473.9174
7	2	6	490.427273	490.4272	490.4270
7	2	5	520.123425	520.1230	520.1232
7	3	5	576.904631	576.9046	576.9043
7	3	4	581.962003	581.9616	581.9617
7	4	4	683.323962	683.3229	683.3235
7	4	3	683.610089	683.6101	683.6096

[a] Reference 13.
[b] Reference 25.

TABLE III—*Continued*

LEVEL			THIS WORK	TOTH et al.	PAPINEAU et al.
7	5	3	818.006858	818.0076	818.0060
7	5	2	818.013860	818.0125	818.0130
7	6	2	981.128585	981.1275	981.1262
7	6	1	981.128663	981.1275	981.1263
7	7	1	1171.530483	1171.5324	1171.5289
7	7	0	1171.530483	1171.5324	1171.5289
8	0	8	512.515764	512.5156	512.5155
8	1	8	513.207114	513.2066	513.2069
8	1	7	598.563052	598.5631	598.5631
8	2	7	609.946469	609.9461	609.9466
8	2	6	653.088798	653.0882	653.0882
8	3	6	701.620415	701.6198	701.6199
8	3	5	711.795403	711.7948	711.7949
8	4	5	808.563369	808.5629	808.5625
8	4	4	809.393440	809.3928	809.3926
8	5	4	942.533021	942.5316	942.5313
8	5	3	942.562785	942.5615	942.5611
8	6	3	1105.004607	1105.0019	1105.0035
8	6	2	1105.005146	1105.0025	1105.0040
8	7	2	1294.837819	1294.8358	1294.8349
8	7	1	1294.837823	1294.8358	1294.8349
8	8	1	1510.866683	1510.8766	1510.8752
8	8	0	1510.866683	1510.8766	1510.8752
9	0	9	634.428228	634.4276	634.4280
9	1	9	634.790973	634.7903	634.7909
9	1	8	735.735262	735.7352	735.7346
9	2	8	743.097408	743.0970	743.0969
9	2	7	801.644353	801.6433	801.6436
9	3	7	841.367896	841.3668	841.3677
9	3	6	859.392843	859.3920	859.3916
9	4	6	949.577991	949.5764	949.5763
9	4	5	951.636239	951.6357	951.6345
9	5	5	1082.786255	1082.7842	1082.7840
9	5	4	1082.887818	1082.8856	1082.8856
9	6	4	1244.439363	1244.4372	1244.4360
9	6	3	1244.442010	1244.4398	1244.4385
9	7	3	1433.575371	1433.5716	1433.5702
9	7	2	1433.575409	1433.5716	1433.5703
9	8	2	1648.943677	1648.9456	1648.9443
9	8	1	1648.943677	1648.9456	1648.9443
9	9	1	1889.426413	1889.4110	1889.5032
9	9	0	1889.426413	1889.4110	1889.5032
10	0	10	768.930232	768.9292	768.9296
10	1	10	769.117036	769.1159	769.1164
10	1	9	885.065115	885.0636	885.0642
10	2	9	889.576124	889.5749	889.5757
10	2	8	964.851521	964.8492	964.8503
10	3	8	995.794211	995.7925	995.7927
10	3	7	1024.569431	1024.5672	1024.5677
10	4	7	1106.265515	1106.2636	1106.2632
10	4	6	1110.760966	1110.7592	1110.7586
10	5	6	1238.796570	1238.7934	1238.7931
10	5	5	1239.091348	1239.0892	1239.0880
10	6	5	1399.453808	1399.4500	1399.4492
10	6	4	1399.464159	1399.4606	1399.4591
10	7	4	1587.745495	1587.7398	1587.7389
10	7	3	1587.745706	1587.7398	1587.7392
10	8	3	1802.337570	1802.3322	1802.3312
10	8	2	1802.337573	1802.3322	1802.3312
10	9	2	2042.049547	2042.0000	
10	9	1	2042.049547	2042.0000	
11	0	11	916.029654	916.0283	916.0286
11	1	11	916.124545	916.1226	916.1239
11	1	10	1046.475428	1046.4739	1046.4738
11	2	10	1049.125294	1049.1240	1049.1238

TABLE III—*Continued*

LEVEL			THIS WORK	TOTH et al.	PAPINEAU et al.
11	2	9	1141.693987	1141.6910	1141.6912
11	3	9	1164.511719	1164.5082	1164.5101
11	3	8	1206.756701	1206.7528	1206.7537
11	4	8	1278.440403	1278.4365	1278.4376
11	4	7	1287.240899	1287.2388	1287.2386
11	5	7	1410.570160	1410.5669	1410.5661
11	5	6	1411.323399	1411.3200	1411.3194
11	6	6	1570.067118	1570.0608	1570.0612
11	6	5	1570.101342	1570.0955	1570.0952
11	7	5	1757.348877	1757.3401	1757.3398
11	7	4	1757.349805	1757.3409	1757.3405
11	8	4	1971.037444	1971.0140	
11	8	3	1971.037460	1971.0140	
12	0	12	1075.716186	1075.7132	1075.7145
12	1	12	1075.763907	1075.7610	1075.7622
12	1	11	1220.031523	1220.0280	1220.0279
12	2	11	1221.539480	1221.5371	1221.5361
12	2	10	1331.222146	1331.2160	1331.2166
12	3	10	1347.124265	1347.1189	1347.1194
12	3	9	1405.130285	1405.1227	1405.1250
12	4	9	1465.833591	1465.8285	1465.8306
12	4	8	1481.447749	1481.4450	1481.4430
12	5	8	1598.073306	1598.0660	1598.0664
12	5	7	1599.805101	1599.8011	1599.7982
12	6	7	1756.293397	1756.2866	1756.2841
12	6	6	1756.392601	1756.3860	1756.3836
12	7	6	1942.383914	1942.3710	1942.3716
12	7	5	1942.387351	1942.3742	1942.3750
12	8	5	2155.029425		2155.0157
12	8	4	2155.029501		2155.0157
13	0	13	1247.967153	1247.9620	1247.9643
13	1	13	1247.990981	1247.9860	1247.9880
13	1	12	1405.823425	1405.8177	1405.8178
13	2	12	1406.661429	1406.6569	1406.6561
13	2	11	1532.742415	1532.7322	1532.7284
13	3	11	1543.252491	1543.2427	1543.2429
13	3	10	1618.710280	1618.6959	1618.6985
13	4	10	1668.103702	1668.0936	1668.0955
13	4	9	1693.450689	1693.4439	1693.4459
13	5	9	1801.215361	1801.2101	1801.2068
13	5	8	1804.847736	1804.8391	1804.8397
13	6	8	1958.136175	1958.1280	1958.1250
13	6	7	1958.394396	1958.3880	
14	0	14	1432.751645	1432.7434	1432.7469
14	1	14	1432.763483	1432.7580	1432.7585
14	1	13	1603.915423	1603.9100	1603.9049
14	2	13	1604.372872	1604.3653	1604.3622
14	2	12	1745.916611	1745.8950	1745.8961
14	3	12	1752.554829	1752.5374	1752.5368
14	3	11	1846.421664	1846.3995	1846.4012
14	4	11	1884.857080	1884.8434	1884.8433
14	4	10	1922.902518	1922.8926	1922.8878
14	5	10	2019.834874	2019.8300	2019.8209
14	5	9	2026.843928	2026.8530	
15	0	15	1630.033055	1630.0180	1630.0235
15	1	15	1630.038918	1630.0280	1630.0294
15	1	14	1814.337393	1814.3200	1814.3192
15	2	14	1814.583740	1814.5640	1814.5654
15	2	13	1970.697589	1970.6600	1970.6554
15	3	13	1974.741099	1974.7150	1974.7078
15	3	12	2087.175427	2087.1376	2087.1367
15	4	12	2115.672938	2115.6330	2115.6438
15	4	11	2169.086502		2169.0613

TABLE III—*Continued*

LEVEL			THIS WORK	TOTH et al.	PAPINEAU et al.
16	0	16	1839.770568	1839.7750	
16	1	16	1839.773466	1839.7790	
16	1	15	2037.091258	2037.0850	2037.0557
16	2	15	2037.222551	2037.2180	
16	2	14	2207.182233		2207.1167
16	3	14	2209.577322		2209.5160
17	0	17	2061.920021	2061.8930	2061.8970
17	1	17	2061.921452	2061.8930	2061.8983
17	1	16	2272.159787		2272.1026
17	2	16	2272.229201		2272.1718
19	0	19	2543.264319		2543.1986
19	1	19	2543.264668		2543.1991

infrared data and the previously available microwave data. The constants which result from these analyses are also shown in Table II.

Although it is difficult to make meaningful comparisons among parameters calculated from large multiparameter fits, especially when these fits use different Hamiltonians, some comments are in order. As would be expected, because our earlier data set is a subset of our current data set, there is generally good agreement between the two sets of constants. The small differences between the higher order terms are traceable to the use of a larger Hamiltonian in this work.

The analysis of Papineau et al. (25) uses our earlier microwave data set in a weighted analysis with their infrared data. The larger calculated uncertainties in the lower-order terms of this analysis are due, presumably, to their somewhat low weighting of the microwave lines relative to the infrared lines. Overall, however, there is generally good agreement between our most recent analysis of microwave data alone, and the mixed analysis of Papineau et al. This agreement is due in no small part to their common data subset, the 56 microwave lines. Toth et al. (13) use the microwave data only to determine the energy of the six lowest rotational energy levels.

Inspection of the experimentally determined infrared energy levels of Toth et al. and Papineau et al. shows them generally to be in very good agreement. It is reasonable to assume that they would provide roughly the same information to an analysis. A possible exception to this is the rather substantial differences that randomly and rarely occur. The most notable are the 9_9 states for which a difference of ~ 0.1 cm^{-1} exists. Thus, since the infrared data sets of these two analyses are very similar, it would appear that the differences between the constants of Toth et al. and ours are due to their use of a smaller number of adjustable parameters and their minimal use of microwave data.

The calculated uncertainties and comparisons among them should be viewed with caution. Heavily weighted microwave lines produce small calculated uncertainties in low-order constants. There is also a tendency of analyses with fewer higher-order constants to produce smaller calculated uncertainties because the correlations among constants are reduced. Thus, it is also interesting to compare the observables, such as energy levels and transition frequencies, that can be calculated from the analyses. Toth et al. have pointed out that if the constants derived from our earlier work (for which the experimental data was restricted to $J \leq 12$, $K \leq 6$) are used to extrapolate

TABLE IV

Observed Microwave Transitions for D_2O (MHz)

TRANSITION	OBSERVED	CALCULATED[a]	O.-C.	STR.[b]	ENERGY[c]	REF.[d]
3(1, 3)- 2(2, 0)	10919.42	10919.41(0.06)	0.01	0.1149	74.1420	46
4(4, 1)- 5(3, 2)	10947.12	10947.18(0.06)	-0.06	0.1151	269.0101	37
8(7, 2)- 9(6, 3)	30182.49	30182.38(0.07)	0.11	0.1945	879.0040	29,6
8(7, 1)- 9(6, 4)	30778.50	30778.50(0.07)	-0.00	0.1945	878.9842	29,6
4(2, 3)- 3(3, 0)	43414.56	43414.64(0.06)	-0.09	0.1328	156.6629	32
4(4, 0)- 5(3, 3)	55482.32	55482.39(0.06)	-0.07	0.1137	267.5305	32
8(5, 4)- 7(6, 1)	70240.63	70240.38(0.06)	0.25	0.2170	668.8408	38,19
8(5, 3)- 7(6, 2)	74471.69	74471.70(0.07)	-0.01	0.2171	668.8402	38,19
6(1, 6)- 5(2, 3)	93350.06	93350.05(0.08)	0.01	0.0952	229.9920	38,19
9(8, 2)-10(7, 3)	103076.40	103076.34(0.08)	0.06	0.1765	1114.7634	38
9(8, 1)-10(7, 4)	103152.89	103152.88(0.08)	0.01	0.1765	1114.7609	38
6(2, 4)- 7(1, 7)	104875.71	104875.67(0.10)	0.04	0.0622	305.7669	38,19
11(2,10)-10(3, 7)	120183.28	120183.27(0.12)	0.01	0.1146	790.8073	19
10(9, 2)-11(8, 3)	145134.80	145134.70(0.09)	0.10	0.1619	1377.5951	39
10(9, 1)-11(8, 4)	145143.82	145143.95(0.09)	-0.13	0.1619	1377.5948	39
4(1, 4)- 3(2, 1)	151710.40	151710.40(0.06)	0.00	0.1614	112.2515	38,19
5(5, 1)- 6(4, 2)	180171.22	180170.92(0.06)	0.30	0.0962	405.5311	38,19
5(1, 5)- 4(2, 2)	181833.02	181833.09(0.07)	-0.07	0.1379	164.1777	38,19
5(5, 0)- 6(4, 3)	187633.10	187633.16(0.06)	-0.06	0.0961	405.2827	38,19
7(4, 4)- 6(5, 1)	192519.44	192519.29(0.06)	0.15	0.2453	485.5979	38,19
12(8, 5)-11(9, 2)	215689.01	215689.03(0.09)	-0.02	0.2959	1518.3918	39
12(8, 4)-11(9, 3)	215731.73	215731.74(0.09)	-0.01	0.2959	1518.3918	39
7(4, 3)- 6(5, 2)	218442.50	218442.59(0.06)	-0.09	0.2464	485.5920	38,19
4(2, 2)- 3(3, 1)	227010.50	227010.33(0.06)	0.17	0.1501	156.6054	38,19
11(3, 8)-12(2,11)	254484.27	254484.27(0.13)	0.01	0.0854	925.5347	19
11(7, 5)-10(8, 2)	265060.07	265059.95(0.08)	0.12	0.3200	1241.7850	19
11(7, 4)-10(8, 3)	265381.30	265381.27(0.09)	0.03	0.3200	1241.7850	19
6(6, 1)- 7(5, 2)	307107.53	307107.48(0.07)	0.05	0.0829	572.1595	38,19
6(3, 4)- 5(4, 1)	307743.14	307743.06(0.06)	0.08	0.2771	331.1234	38,19
6(6, 0)- 7(5, 3)	308133.65	308133.49(0.07)	0.17	0.0829	572.1253	38,19
1(1, 0)- 1(0, 1)	316799.81	316799.88(0.04)	-0.07	1.5000	12.1170	38,19
5(2, 4)- 4(3, 1)	339035.26	339035.28(0.07)	-0.02	0.2831	206.2765	38
10(6, 5)- 9(7, 2)	345039.17	345039.28(0.07)	-0.11	0.3488	991.2184	*
10(6, 4)- 9(7, 3)	347278.23	347278.33(0.07)	-0.10	0.3489	991.2179	*
7(2, 5)- 8(1, 8)	393332.82	393332.84(0.12)	-0.01	0.0421	388.1421	*
7(7, 1)- 8(6, 2)	403251.62	403251.74(0.07)	-0.13	0.0730	767.6977	*
7(7, 0)- 8(6, 3)	403377.36	403377.50(0.07)	-0.14	0.0730	767.6935	*
2(1, 1)- 2(0, 2)	403561.82	403561.90(0.04)	-0.08	2.1632	35.8780	6
10(2, 9)- 9(3, 6)	428706.47	428706.45(0.10)	0.02	0.1622	659.4119	*
6(3, 3)- 5(4, 2)	430949.26	430949.25(0.07)	0.01	0.2882	331.0717	*
9(5, 5)- 8(6, 2)	452326.48	452326.50(0.08)	-0.02	0.3835	767.6977	*
3(1, 2)- 2(2, 1)	458531.45	458531.28(0.06)	0.17	0.2671	73.6764	6
9(5, 4)- 8(6, 3)	466238.74	466238.63(0.08)	0.11	0.3841	767.6935	*
2(0, 2)- 1(1, 1)	468246.57	468246.58(0.05)	-0.01	0.7021	20.2590	6
8(8, 1)- 9(7, 2)	469619.17	469619.14(0.09)	0.03	0.0654	991.2184	*
8(8, 0)- 9(7, 3)	469633.53	469633.50(0.09)	0.03	0.0654	991.2179	*
3(1, 2)- 3(0, 3)	555330.36	555330.20(0.05)	0.16	2.4137	70.4475	*
8(4, 5)- 7(5, 2)	571220.05	571220.10(0.09)	-0.05	0.4230	572.1595	*
6(2, 5)- 5(3, 2)	572114.91	572114.93(0.07)	-0.02	0.3809	269.0101	*
1(1, 1)- 0(0, 0)	607349.60	607349.61(0.06)	-0.01	1.0000	0.0000	19,47
9(2, 8)- 8(3, 5)	642615.95	642616.02(0.09)	-0.07	0.2339	540.8796	*
8(4, 4)- 7(5, 3)	643247.42	643247.39(0.11)	0.03	0.4287	572.1253	*
7(3, 5)- 6(4, 2)	649560.46	649560.51(0.08)	-0.05	0.4501	405.5311	*
4(2, 2)- 4(1, 3)	692243.60	692243.56(0.07)	0.05	3.5561	141.0869	*
3(2, 1)- 3(1, 2)	697922.72	697922.62(0.06)	0.11	2.3689	88.9713	*
7(2, 6)- 6(3, 3)	714087.25	714087.24(0.08)	0.02	0.3882	345.4466	*
5(2, 3)- 4(3, 2)	722669.85	722669.93(0.08)	-0.08	0.3857	205.8863	*
8(2, 7)- 7(3, 4)	740648.84	740648.76(0.09)	0.08	0.3216	436.0596	*
2(2, 0)- 2(1, 1)	743563.43	743563.46(0.06)	-0.03	1.1701	49.3394	*
5(2, 3)- 5(1, 4)	751110.67	751110.78(0.07)	-0.11	4.4195	204.9376	*
4(1, 3)- 4(0, 4)	782470.88	782471.20(0.06)	-0.32	2.3521	114.9865	*
3(0, 3)- 2(1, 2)	850757.72	850757.58(0.05)	0.14	1.6140	42.0693	*
6(2, 4)- 6(1, 5)	890396.08	890396.03(0.12)	0.06	4.7667	279.5647	*
2(1, 2)- 1(0, 1)	897947.11	897947.22(0.07)	-0.12	1.5000	12.1170	*
4(1, 3)- 3(2, 2)	930942.47	930942.62(0.06)	-0.15	0.7159	110.0340	*
2(2, 1)- 2(1, 2)	947556.57	947556.50(0.06)	0.06	0.8333	42.0693	*
3(2, 2)- 3(1, 3)	1065097.24	1065097.11(0.06)	0.12	1.3277	74.5062	*

[a] Uncertainty in calculated frequency as per discussion in reference 1.
[b] Line strength calculated as discussed in reference 45.
[c] Energy of lower state in reciprocal cm.
[d] * this work.

to the edge of their infrared data set ($J \leq 19$, $K \leq 9$), differences as great as 0.6 cm^{-1} occur at $10_{9,1}$. Table III shows the *observed* infrared levels of both Toth *et al.* and Papineau *et al.* as well as the energy levels *calculated* from our new analysis of the microwave lines. Careful inspection of this table shows that our new analysis predicts these levels very well and is in general comparable with the residuals of the *fit* of Toth *et al.* to their infrared data set. Papineau *et al.* do not publish the residuals of their fit, but they are presumably smaller because they have included more adjustable parameters. Toth *et al.* could also have reduced their residuals by including more parameters.

On the other hand, as would be expected, our microwave analysis much more accurately predicts the pure rotational spectrum of HDO in the region below 1 THz. For lines in the analysis (this includes the vast majority of the lines with significant absorption below 1 THz) our analysis predicts these lines to a fraction of a MHz. No check is possible for lines we have not observed, but it is to be expected that similar transitions would be well predicted (≤ 1 MHz), but that lines far removed in quantum number would be poorly predicted. By comparison of the frequencies of our newly observed lines with the predictions based upon the energy levels of Toth *et al.* and of Papineau *et al.*, it would appear that their quoted uncertainties are realistic.

TABLE V

Spectral Constants of D$_2$O (MHz)

Constant	This Work value	2σ	Steenbeckliers and Bellet[a] value	2σ	Lin and Shaw[b] value	2σ	Papineau et al.[c] value	2σ
A	462279.013	0.118	462278.85	0.05	462266.8	5.7	462278.942	0.078
B	218038.411	0.068	218038.23	0.03	218030.6	2.4	218038.288	0.039
C	145257.995	0.047	145258.02	0.02	145256.6	1.7	145258.006	0.012
Δ_J	9.303832	0.0024	9.2879	0.0150	8.8894	0.0342	9.2931	0.0014
Δ_{JK}	-45.69569	0.0108	-45.721	0.021	-47.448	0.195	-45.666	0.008
Δ_K	277.44893	0.0084	277.42	0.03	276.43	0.17	277.41	0.01
δ_J	3.6939628	0.0009	3.6877	0.0006	3.6281	0.0090	3.6907	0.0004
δ_K	10.4649	0.0124	10.42	0.03	9.150	0.198	10.405	0.009
H_J	$(0.243353\ 0.0042)\times10^{-2}$		$(0.174\ 0.002)\times10^{-2}$		$(-0.546\ 0.117)\times10^{-3}$		$(0.1953\ 0.0014)\times10^{-2}$	
H_{JK}	$(-0.47698\ 0.0372)\times10^{-2}$		$(-0.776\ 0.042)\times10^{-2}$		$(-0.244\ 0.020)\times10^{-1}$		$(-0.6445\ 0.0171)\times10^{-2}$	
H_{KJ}	$(-0.7480502\ 0.0056)\times10^{-1}$		$(-0.7862\ 0.0057)\times10^{-1}$		$(-0.791\ 0.087)\times10^{-1}$		$(-0.7367\ 0.0048)\times10^{-1}$	
H_K	0.55778200	0.0006	0.5553	0.0004	0.5210	0.0054	0.5531	0.0004
h_J	$(0.104876\ 0.0012)\times10^{-2}$		$(0.905\ 0.006)\times10^{-3}$		$(0.4509\ 0.0393)\times10^{-3}$		$(0.9672\ 0.0060)\times10^{-3}$	
h_{JK}	$(0.26465\ 0.0340)\times10^{-2}$		$(-0.266\ 0.017)\times10^{-2}$		$(-0.4512\ 0.1067)\times10^{-2}$		$(-0.1586\ 0.0084)\times10^{-2}$	
h_K	0.111690	0.0010	0.1182	0.0013	$(-0.207\ 0.157)\times10^{-1}$		0.1136	0.0011
L_J	$(-0.526382\ 0.0282)\times10^{-5}$						$(-0.5045\ 0.0390)\times10^{-6}$	
L_{JJK}	$(-0.502095\ 0.0398)\times10^{-4}$						$(0.1642\ 0.0030)\times10^{-5}$	
L_{JK}			$(-0.154\ 0.016)\times10^{-3}$		$(0.1450\ 0.0025)\times10^{-2}$		$(-0.1154\ 0.0132)\times10^{-3}$	
L_{KKJ}			$(0.612\ 0.042)\times10^{-3}$		$(-0.3768\ 0.0016)\times10^{-2}$		$(0.4544\ 0.0360)\times10^{-3}$	
L_K	$(-0.1587482\ 0.0010)\times10^{-2}$		$(-0.1923\ 0.0029)\times10^{-2}$		$(0.1642\ 0.0029)\times10^{-2}$		$(-0.1788\ 0.0029)\times10^{-2}$	
ℓ_J	$(-0.10352\ 0.0082)\times10^{-5}$						$(-0.2507\ 0.0198)\times10^{-6}$	
ℓ_{JK}	$(-0.410456\ 0.0260)\times10^{-4}$							
ℓ_{KJ}	$(-0.156585\ 0.0092)\times10^{-3}$							
ℓ_K	$(-0.151122\ 0.0068)\times10^{-3}$		$(-0.660\ 0.042)\times10^{-3}$		$(0.4035\ 0.0060)\times10^{-2}$		$(-0.5205\ 0.0360)\times10^{-3}$	
P_{KKJ}			$(-0.13\ 0.03)\times10^{-6}$		$(-0.2358\ 0.0143)\times10^{-5}$			
P_K	$(0.472394\ 0.0102)\times10^{-5}$		$(0.4991\ 0.0063)\times10^{-5}$		$(-0.7747\ 0.0905)\times10^{-7}$		$(0.4547\ 0.0096)\times10^{-5}$	
T_K	$(-0.936711\ 0.044)\times10^{-8}$		$(-0.980\ 0.021)\times10^{-8}$		$(-0.4332\ 0.1850)\times10^{-8}$		$(-0.8591\ 0.0420)\times10^{-8}$	
rms MW	0.128		0.160		---		0.127	
rms IR	---		---		1199		32.9	

[a] Reference 6. The P^4 constants given here were taken from reference 48.
[b] Reference 48.
[c] Reference 24.

TABLE VI

Observed Microwave Transitions for D_2O in the ν_2 Excited Bending Mode (MHz)

TRANSITION	OBSERVED	CALCULATED[a]	O.-C.	PREDICTED[b]	O.-P.	STR.[c]	ENERGY[d]	REF.[e]
4(1, 4)- 3(2, 1)	29695.58	29695.39(0.15)	0.19	29695.06(0.20)	0.52	0.1731	117.0475	6
5(2, 3)- 6(1, 6)	50538.74	50538.86(0.17)	-0.12	50539.39(0.34)	-0.65	0.1108	233.2919	6
5(1, 5)- 4(2, 2)	51436.54	51436.78(0.13)	-0.24	51436.99(0.14)	-0.45	0.1547	169.0144	6
4(2, 2)- 3(3, 1)	54216.53	54216.41(0.16)	0.12	54216.09(0.30)	0.45	0.1474	167.2059	6
6(5, 2)- 7(4, 3)	66958.41	66958.44(0.19)	-0.03	66960.23(1.37)	-1.82	0.2443	511.3825	6
6(3, 4)- 5(4, 1)	79170.08	79169.99(0.17)	0.09	79169.72(0.34)	0.36	0.2761	349.5818	6
5(2, 4)- 4(3, 1)	169894.01	169894.12(0.14)	-0.11	169894.26(0.22)	-0.25	0.2875	216.8908	*
6(3, 3)- 5(4, 2)	193023.09	193023.14(0.17)	-0.05	193023.30(0.37)	-0.21	0.2848	349.5379	*
4(4, 1)- 5(3, 2)	244879.03	244878.92(0.16)	0.10	244878.69(0.29)	0.34	0.1139	279.6069	*
6(2, 4)- 7(1, 7)	269656.05	269656.02(0.19)	0.02	269653.01(1.91)	3.04	0.0739	305.5774	*
4(4, 0)- 5(3, 3)	285640.48	285640.50(0.16)	-0.03	285640.56(0.31)	-0.08	0.1129	278.2522	*
8(4, 5)- 7(5, 2)	290261.31	290261.37(0.18)	-0.05	290262.16(0.72)	-0.84	0.4208	600.2803	*
8(4, 4)- 7(5, 3)	352239.57	352239.55(0.19)	0.02	352238.24(1.50)	1.34	0.4251	600.2531	*
1(1, 0)- 1(0, 1)	354717.83	354717.97(0.10)	-0.14	354718.02(0.12)	-0.19	1.5000	12.1270	*
3(1, 2)- 2(2, 1)	363629.65	363629.74(0.15)	-0.09	363629.90(0.27)	-0.25	0.2587	78.4757	*
6(2, 5)- 5(3, 2)	406703.03	406703.02(0.18)	0.01	406702.94(0.54)	0.09	0.3976	279.6069	*
7(3, 5)- 6(4, 2)	424737.31	424737.27(0.18)	0.03	424736.97(0.61)	0.34	0.4522	424.0342	*
2(0, 2)- 1(1, 1)	434820.73	434820.70(0.13)	0.03	434820.68(0.20)	0.05	0.6877	21.4142	*
2(1, 1)- 2(0, 2)	444777.95	444777.81(0.09)	0.15	444777.76(0.11)	0.19	2.1871	35.9183	*
3(1, 2)- 3(0, 3)	601404.71	601404.75(0.18)	-0.04	601405.08(0.55)	-0.37	2.4804	70.5443	*
1(1, 1)- 0(0, 0)	641981.99	641981.95(0.15)	0.04	641981.87(0.29)	0.12	1.0000	0.0000	*

[a] Uncertainty in calculated frequency as per discussion in reference 1.
[b] Predicted from an analysis which did not contain the observed frequency as a data point.
[c] Line strength calculated as discussed in reference 45.
[d] Energy of lower state in reciprocal cm.
[e] * this work. Reference 6 has a discussion of previous work.

B. Ground State of D_2O

A number of workers have contributed to the previously known microwave data set for D_2O of 36 transitions (6, 19, 29, 37–41, 46, 47). In this work, we report 33 additional transitions, predominately in the region 500–1100 GHz, and a detailed analysis. The entire data set is shown in Table IV. The new lines are indicated with a *. The spectral constants which result from this analysis are shown in Table V. Also shown in this table are the results of an analysis of Steenbeckliers and Bellet (6) of the 36 microwave lines plus the infrared data available to them. This table also includes constants derived by Lin and Shaw (48) from their infrared work and the 36 microwave lines, and a recent analysis by Papineau et al. (24), who analyzed extensive new infrared D_2O data along with the 36 microwave lines. D_2O has also been analyzed by Benedict et al. (19) who used a weighted data set of 29 microwave lines and infrared data and the Hamiltonian of Kneizys et al. (20). Since this Hamiltonian is fundamentally different, it is not possible to include their results in our comparison.

As for HDO, it is difficult to make comparisons among analyses that use different Hamiltonian terms and different data sets. However, all of these analyses include heavily weighted microwave lines, and it might be expected that the constants would be quite similar. In fact, there is substantially more variation among them than among the HDO analyses. It would appear that this is in part due to the lack of a-type transitions in D_2O. The lack of a-type transitions also makes calculation of energy levels from centrifugal distortion models substantially less accurate. A "worst case" comparison between extrapolations based upon centrifugal distortion of the microwave analysis and direct observations by infrared techniques shows this. For example,

comparing the results of our current analysis with those of Papineau et $al.$ (24), for the level $12_{10,2}$ we obtain 1819.9469 cm^{-1}, while they obtain 1821.1487 cm^{-1}, a difference of about 1.2 cm^{-1}. However, for states more closely related to the microwave data set, the results of the two analyses are much closer. For the level $8_{6,2}$, we obtain 767.6978 cm^{-1}, while Papineau et $al.$ obtain 767.7207 cm^{-1}, a difference of only about 0.02 cm^{-1}.

If the energy levels that Papineau et $al.$ derived from their infrared data and the previously available microwave data are used to calculate the transition frequencies of our new submillimeter observations, the difference between the observed and calculated frequencies range from the round off of their table (3 MHz) for lines similar to the previously available microwave data, to 40 MHz for higher J or K lines. This latter number is consistent with the rms deviation of the infrared lines in their fit (33 MHz).

TABLE VII

Spectral Constants for D_2O in the ν_2 Excited Bending Mode[a]

Constant	This Work value	2σ	Steenbeckliers and Bellet[b] value	2σ	Lin and Shaw[c] value	2σ
A	498675.977	0.341	498730	24	498702	19
B	220008.148	0.252	220039	14	220008	11
C	143591.670	0.117	143611	6	143594	9
Δ_J	10.07613	0.010	10.220	0.093	9.673	0.023
Δ_{JK}	-57.0135	0.071	-55.9	1.7	-55.57	0.42
Δ_K	420.8700	0.042	418.5	1.2	418.66	0.81
δ_J	4.093022	0.004	4.152	0.045	4.014	0.053
δ_K	22.3051	0.048	21.0	1.5	20.46	0.20
H_J	$(0.26758 \quad 0.015) \times 10^{-2}$		*		*	
H_{JK}	$(0.6843 \quad 0.437) \times 10^{-2}$		*		$(-0.253 \quad 0.019) \times 10^{-1}$	
H_{KJ}	-0.167585	0.004	*		$(-0.234 \quad 0.047) \times 10^{-1}$	
H_K	1.27712	0.004	1.049	0.030	0.9348	0.0078
h_J	$(0.12115 \quad 0.007) \times 10^{-2}$		*		$(0.356 \quad 0.143) \times 10^{-3}$	
h_{JK}	*		*		*	
h_K	0.25163	0.009	*		*	
L_J	*		---		---	
L_{JJK}	*		---		---	
L_{JK}	---		*		$(0.1331 \quad 0.0024) \times 10^{-2}$	
L_{KKJ}	---		*		$(-0.3570 \quad 0.0037) \times 10^{-2}$	
L_K	$(-0.44170 \quad 0.006) \times 10^{-2}$		*		$(0.1577 \quad 0.0001) \times 10^{-2}$	
ℓ_J	*		---		---	
ℓ_{JK}	*		---		---	
ℓ_{KJ}	*		---		---	
ℓ_K	*		*		$(0.3817 \quad 0.0010) \times 10^{-2}$	
P_{KKJ}	---		*		*	
P_K	*		*		$(0.618 \quad 0.029) \times 10^{-5}$	
T_K	*		*		*	
rms MW	0.189		---		---	
rms IR	---		---		1199	

[a]* indicates that the constant was fixed at the ground state value. See Table V.
[b]Reference 6. The P^4 constants given here were taken from reference 48.
[c]Reference 48.

C. ν_2 State of D_2O

The ν_2 band of $D_2{}^{16}O$ lies at about 1200 cm^{-1} above the ground state. Thus, at ambient temperatures its pure rotational spectrum is about 400 times weaker than that of its ground state. However, the combination of the sensitivity of our experimental technique and the relatively strong spectrum of D_2O have allowed us to observe 15 new lines. These, plus the 6 lines previously reported by Steenbeckliers and Bellet (6), make possible a centrifugal distortion analysis. Table VI shows the complete microwave data set.

Because D_2O is such a light molecule, the number of distortion parameters required to characterize its spectrum to microwave accuracy is large. For example, the ground vibrational states of D_2O and HDO required 24 and 28 constants, respectively. The number of constants required to fit D_2O and HDO in the ground state is greater than the number of microwave data points in the excited vibrational state of D_2O. Therefore, we have analyzed the excited state of D_2O by fixing a number of the parameters to values obtained for the ground state. In general, these fixed parameters were the higher-order parameters, but the rapid change of those parameters associated with the bending motion (e.g., H_K, L_K, etc.) required that they be left as adjustable parameters. The results of this analysis are shown in Table VII, along with the results of Steenbeckliers and Bellet (6) and Lin and Shaw (48), who include extensive infrared data. Since the redundancy of our fit is small, we have taken several precautions to guard against the inclusion of missassigned lines and to show the statistical validity of the analysis. Table VI also shows the results of 21 separate analyses. In each of the analyses, one line has been removed from the data set and predicted from the remaining data. Inspection of this table shows that the predictions are very good. In addition, Worchesky et al. (49) have made, in a very nice heterodyne experiment, high-precision diode laser measurements of a number of lines of the ν_2 band. Table VIII shows the band center of ν_2 as derived from these measurements and our calculated ground state and excited state energy levels. This is an especially stringent test because

TABLE VIII

Vibrational Frequency of ν_2 Calculated from Diode Laser Results and the Rotational Analyses of D_2O (cm^{-1})

Transition	Observed[a] Frequency	Rotational[b] Contribution	Vibrational[c] Frequency
6(6, 0) - 5(5, 1) 6(6, 1) - 5(5, 0)	1035.4343	-142.9397	1178.3740
7(3, 4) - 6(2, 5)	1035.4921	-142.8866	1178.3787
11(3, 9) - 10(2, 8)	1048.7007	-129.6659	1178.3666
12(2,10) - 11(3, 9)	1053.9497	-124.4147	1178.3644
10(1, 9) - 9(2, 8)	1073.2597	-105.1165	1178.3762
5(3, 3) - 4(2, 2)	1079.8632	-98.5161	1178.3793
10(2, 9) - 10(1,10)	1084.6568	-93.7207	1178.3775
9(0, 9) - 8(1, 8)	1085.7458	-92.6323	1178.3781

[a] From reference 49.

[b] Calculated from the analyses of the pure microwave data in this work.

[c] Average calculated vibrational frequency = 1178.3743 cm^{-1}.

TABLE IX

Observed Microwave Transitions in the ν_2 Excited Bending Mode of HDO and H_2O (MHz)

HDO			H_2O		
Transition	Frequency	Ref.[a]	Transition	Frequency	Ref.
2(2,0)-2(2,1)	10557.45	42	4(2,2)-5(1,5)	2159.98	50
5(3,2)-5(3,3)	21820.34	42	4(2,3)-3(3,0)	12008.80	52
6(2,5)-5(3,2)	27892.29	42	5(3,2)-4(4,1)	26834.27	52
3(2,1)-3(2,2)	51675.47	42	4(1,4)-3(2,1)	67803.96	51
6(3,3)-6(3,4)	63155.55	42	4(4,0)-5(3,3)	96261.16	52
3(1,2)-2(2,1)	67153.04	42	2(2,0)-3(1,3)	119995.94	52
2(0,2)-1(1,1)	434517.71	*	1(1,0)-1(0,1)	658006.50	15
1(0,1)-0(0,0)	466402.00	*			
1(1,0)-1(0,1)	574366.78	*			
2(1,1)-2(0,2)	671641.75	*			

[a] *, this work.

our analyses must calculate both the upper and lower state energy levels by extrapolation. Inspection of this table shows that the individual calculations of the vibrational frequency are in remarkably good agreement. The average of 1178.3743 cm^{-1} is in good agreement with the value of 1178.3794 ± 0.0025 observed by Lin and Shaw (48).

We have also observed a few lines in the ν_2 bending modes of HDO and H_2O. These measured frequencies are shown in Table IX, along with the previously known microwave lines of HDO and H_2O in the ν_2 bending mode. For both of these species, too few data points exist for a meaningful analysis at this time. To help ensure against

TABLE X

Observed Microwave Transitions in the Ground State H_2O (MHz)

Transition	Frequency	Ref.[a]
6(1,6)- 5(2, 3)	22235.08	53,54
3(1,3)- 2(2, 0)	183310.12	55,56
10(2,9)- 9(3, 6)	321225.64	5
5(1,5)- 4(2, 2)	325152.92	57,5
4(1,4)- 3(2, 1)	380197.37	57,5
10(3,7)-11(2,10)	390134.51	15
7(5,3)- 6(6, 0)	437346.67	5
6(4,3)- 5(5, 0)	439150.81	5
7(5,2)- 6(6, 1)	443018.30	5
4(2,3)- 3(3, 0)	448001.08	57,5
6(4,2)- 5(5, 1)	470888.95	5
5(3,3)- 4(4, 0)	474689.13	5
6(2,4)- 7(1, 7)	488491.13	5
8(6,3)- 7(7, 0)	503568.53	15
8(6,2)- 7(7, 1)	504482.69	15
1(1,0)- 1(0, 1)	556936.00	47,5
5(3,2)- 4(4, 1)	620700.81	5
9(7,3)- 8(8, 0)	645766.01	58
9(7,2)- 8(8, 1)	645905.62	58
2(1,1)- 2(0, 2)	752033.23	5
4(2,2)- 3(3, 1)	916171.58	15
5(2,4)- 4(3, 1)	970315.02	15
2(0,2)- 1(1, 1)	987926.76	15

[a] Only the references for the first microwave observation of each line, and the most precise measurement (listed in the frequency column), are given.

the measurement of impurity lines, each of the lines we observed has been measured from at least two different harmonics, and the frequencies checked against all known lines of isotopic water. However, the surety of these lines is necessarily less than that for the other lines reported by us in this paper.

We have also recently reported (*15*) new observations in the ground state spectrum of H_2O. These, along with earlier measurements (*5*) and two newly observed transitions by Burenin *et al.* (*58*), are shown in Table X.

V. CONCLUSIONS

The measurements reported in this paper represent more than a third of all of the microwave lines of the major isotopes of water that have now been reported in the literature. Many of the previously reported lines resulted from our earlier work. These new lines result primarily from the extension of our experimental methods into the Terahertz region and the measurement of weaker, more highly excited, transitions. The analyses of HDO and D_2O should provide accurate calculations of all ground state pure rotational transitions of significant strength to well beyond 1 THz. These calculations are available upon request. For H_2O, all of the strong lines below 1 THz have been measured directly.

The results of our analyses have been compared with earlier analyses that were based on weighted fits of the previously available microwave data and infrared data. Comparisons were also made with experimentally determined energy levels. For HDO, deviations between our calculated levels and the experimentally determined levels only become significant for the most highly excited levels. For levels within the range of the microwave data, the agreement was within the expected experimental uncertainty. For D_2O, the lack of *a*-type transitions caused those levels that depended upon model extrapolation to be in poorer agreement with the experimental energy levels.

REFERENCES

1. P. HELMINGER, R. L. COOK, AND F. C. DE LUCIA, *J. Mol. Spectrosc.* **40**, 125–138 (1971).
2. F. C. DE LUCIA, R. L. COOK, P. HELMINGER, AND W. GORDY, *J. Chem. Phys.* **55**, 5334–5339 (1971).
3. P. HELMINGER, R. L. COOK, AND F. C. DE LUCIA, *J. Chem. Phys.* **56**, 4581–4584 (1972).
4. R. L. COOK, F. C. DE LUCIA, AND P. HELMINGER, *J. Mol. Spectrosc.* **41**, 123–136 (1972).
5. F. C. DE LUCIA, P. HELMINGER, R. L. COOK, AND W. GORDY, *Phys. Rev. A* **5**, 487–490 (1972).
6. G. STEENBECKLIERS AND J. BELLET, *J. Mol. Spectrosc.* **45**, 10–34 (1973).
7. W. BAUMANN AND R. MECKE, *Z. Physik* **81**, 445–464 (1933).
8. H. M. RANDALL, D. M. DENNISON, N. GINSBURG, AND L. R. WEBER, *Phys. Rev.* **52**, 160–174 (1937).
9. W. S. BENEDICT, N. M. GALILAR, AND F. K. PLYLER, *J. Chem. Phys.* **24**, 1139–1165 (1956).
10. See, for example, J.-M. FLAUD AND C. CAMY-PEYRET, *J. Mol. Spectrosc.* **51**, 142–150 (1974); J.-M. FLAUD, C. CAMY-PEYRET, AND J.-P. MAILLARD, *Mol. Phys.* **32**, 499–521 (1976); C. CAMY-PEYRET AND J.-M. FLAUD, *Mol. Phys.* **32**, 523–537 (1976).
11. G. GUELACHVILI, *Nouv. Rev. Opt. Appl.* **3**, 317–336 (1972).
12. J. KAUPPINEN, T. KÄRKKÄINEN, AND E. KYRÖ, *J. Mol. Spectrosc.* **71**, 15–44 (1978).
13. R. A. TOTH, V. D. GUPTA, AND J. W. BRAULT, *Appl. Opt.* **21**, 3337–3347 (1982).
14. R. H. PARTRIDGE, *J. Mol. Spectrosc.* **87**, 429–437 (1981).
15. P. HELMINGER, J. K. MESSER, AND F. C. DE LUCIA, *Appl. Phys. Lett.* **42**, 309–310 (1983).
16. W. C. KING AND W. GORDY, *Phys. Rev.* **90**, 319–320 (1953).
17. P. HELMINGER, F. C. DE LUCIA, AND W. GORDY, *Phys. Rev. Lett.* **25**, 1397–1399 (1970).

18. J. K. G. WATSON, *J. Chem. Phys.* **46**, 1935–1949 (1967).
19. W. S. BENEDICT, S. A. CLOUGH, L. FRENKEL, AND T. E. SULLIVAN, *J. Chem. Phys.* **53**, 2565–2570 (1970).
20. F. X. KNEIZYS, J. N. FREEDMAN, AND S. A. CLOUGH, *J. Chem. Phys.* **44**, 2552–2556 (1966).
21. C. CAMY-PEYRET, J.-M. FLAUD, G. GUELACHVILI, AND C. AMOIT, *Mol. Phys.* **26**, 825–855 (1973).
22. J.-M. FLAUD AND C. CAMY-PEYRET, *Mol. Phys.* **26**, 811–823 (1973).
23. C. CAMY-PEYRET AND J.-M. FLAUD, *J. Mol. Spectrosc.* **59**, 327–337 (1976).
24. N. PAPINEAU, J.-M. FLAUD, C. CAMY-PEYRET, AND G. GUELACHVILI, *J. Mol. Spectrosc.* **87**, 219–232 (1981).
25. N. PAPINEAU, C. CAMY-PEYRET, J.-M. FLAUD, AND G. GUELACHVILI, *J. Mol. Spectrosc.* **92**, 451–468 (1982).
26. M. W. P. STRANDBERG, T. WENTINK, R. E. HILLGER, G. H. WANNIER, AND M. L. DEUTSCH, *Phys. Rev.* **73**, 188 (1948).
27. M. W. P. STRANDBERG, *J. Chem. Phys.* **17**, 901–904 (1949).
28. Y. BEERS AND S. WEISBAUM, *Phys. Rev.* **91**, 1014 (1953).
29. C. K. JEN, D. R. BIANCO, AND J. T. MASSEY, *J. Chem. Phys.* **21**, 520–525 (1953).
30. D. W. POSENER AND M. W. P. STRANDBERG, *J. Chem. Phys.* **21**, 1401–1402 (1953).
31. S. WEISBAUM, Y. BEERS, AND G. HERMANN, *J. Chem. Phys.* **23**, 1601–1605 (1955).
32. G. ERLANDSSON AND J. COX, *J. Chem. Phys.* **25**, 778–779 (1956).
33. E. B. TREACY AND Y. BEERS, *J. Chem. Phys.* **36**, 1473–1480 (1961).
34. D. W. POSENER, *Aust. J. Phys.* **10**, 276–285 (1957).
35. P. THADDEUS, L. C. KRISHER, AND J. H. N. LOUBSER, *J. Chem. Phys.* **40**, 257–273 (1964).
36. H. BLUYSSEN, J. VERHOEVEN, AND A. DYMANUS, *Phys. Lett. A* **25**, 214–215 (1967).
37. J. VERHOEVEN, H. BLUYSSEN, AND A. DYMANUS, *Phys. Lett. A* **26**, 424–425 (1968).
38. G. STEENBECKLIERS AND J. BELLET, *Comp. Rend. B* **270**, 1039–1041 (1970).
39. J. BELLET AND G. STEENBECKLIERS, *Comp. Rend. B* **271**, 1208–1211 (1970).
40. G. STEENBECKLIERS, private communications.
41. J. BELLET, private communications.
42. W. LAFFERTY, J. BELLET, AND G. STEENBECKLIERS, *Comp. Rend. B* **273**, 388–391 (1971).
43. D. R. JOHNSON, private communication.
44. C. H. TOWNES AND F. R. MERRITT, *Phys. Rev.* **70**, 558–559 (1946).
45. J. K. MESSER, FRANK C. DE LUCIA, AND PAUL HELMINGER, *Int. J. Inf. MM. Waves* **4**, 505–539 (1983).
46. H. J. BLUYSSEN, Thesis, Nijmegen (1968).
47. D. A. STEPHENSON AND R. G. STRAUCH, *J. Mol. Spectrosc.* **35**, 494–495 (1970).
48. C. L. LIN AND J. H. SHAW, *J. Mol. Spectrosc.* **66**, 441–447 (1977).
49. T. L. WORCHESKY, K. J. RITTER, J. P. SUTTER, AND W. A. RIESSLER, *Opt. Lett.* **2**, 70–71 (1978).
50. M. HERMAN, J. W. C. JOHNS, AND A. R. W. MCKELLAR, *Canad. J. Phys.* **57**, 397–401 (1979).
51. G. STEENBECKLIERS AND J. BELLET, *Comp. Rend. B* **273**, 471–474 (1971).
52. H. KUZE, *Astrophys. J.* **239**, 1131–1133 (1980).
53. G. E. BECKER AND S. H. AUTLER, *Phys. Rev.* **70**, 300–307 (1946).
54. S. G. KUKOLICH, *J. Chem. Phys.* **50**, 3751–3755 (1969).
55. W. C. KING AND W. GORDY, *Phys. Rev.* **93**, 407–412 (1954).
56. R. S. WINTON, Ph.D. dissertation, Duke University, 1972.
57. M. LICHENSTEIN, V. E. DERR, AND J. J. GALLAGHER, *J. Mol. Spectrosc.* **20**, 391–401 (1966).
58. A. V. BURENIN, T. M. FEVRAL'SKIKH, E. N. KARYAKIN, O. L. POLYANSKY, AND S. M. SHAPIN, *J. Mol. Spectrosc.* **100**, 182–192 (1983).