A New Analysis of the Rotational Spectrum of CH_3OD

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Using an extended version of the internal axis method previously introduced to analyze the rotational spectrum of methanol to microwave accuracy, we have reanalyzed new and existing data for CH_3OD in the three lowest torsional levels ($v_t = 0, 1, 2$). As in the case of CH_3OH, we have succeeded in fitting the spectrum to the accuracy of our experiment (50–100 kHz) by dividing the data into two sets according to the symmetry species (A or E) of the torsional sublevels, and by adding a number of terms to the Hamiltonian to describe to high order the interaction between torsional motion and end-over-end rigid body rotation. Specifically, 226 transitions in the A symmetry levels and 246 transitions in the E symmetry levels involving rotational quantum number $J \leqslant 9$ were fit to root-mean-square deviations of 81 and 92 kHz, respectively. © 1993 Academic Press, Inc.

I. INTRODUCTION

The torsional–rotational spectroscopy of the internal rotor methanol has been studied by a large number of investigators [see, e.g., (*1, 2*) and references therein.] For the last decade, we have measured transitions in methanol up to 1 THz in frequency and have progressively improved our analysis of the spectrum using an extended version of the internal axis method (IAM) (*1–4*) as formulated by Lees and Baker (*5*). The analogous spectra of the isotopomers $^{13}CH_3OH$ (*4, 6–8*) and CH_3OD (*9*) have also been studied in this fashion. The spectral lines measured in our laboratory involve changes in rotational levels only, for molecules in both the A and the E symmetry substates of the three lowest torsional levels ($v_t = 0, 1, 2$). A voluminous number of far-infrared transition frequencies involving both pure rotational and torsional–rotational transitions have been measured and analyzed by Moruzzi and co-workers (*10–12*).

Although our earliest analysis of the rotational spectrum of methanol fit the spectrum to a root-mean-square (rms) deviation of 1.2 MHz, roughly 10 times our experimental accuracy (*1*), more recent analyses of both normal methanol and its C-13 isotopomer have fit spectra involving rotational quantum number J as large as 24 to experimental accuracy (*2–4, 8*). The improvements in our analysis stem from several factors. First, we have divided the transitions into distinct sets belonging to the two torsional symmetry species—A and E. Second, a large number of spectroscopic parameters have

been added to the Hamiltonian to describe the interaction between torsional motion and end-over-end rigid body rotation. Finally, the data sets were rigorously checked for incorrect assignments by loop methods, when possible, and by so-called "error curve" techniques when loops were not available. Our current analyses of CH_3OH and $^{13}CH_3OH$ are sufficiently tight to allow accurate prediction of large numbers of unmeasured transitions through 1 THz in frequency (4). Both our measurements and our predictions have been utilized by radioastronomers to study numerous transitions of methanol in interstellar space (13).

The analysis of the isotopomer CH_3OD has not progressed to the same extent. Our previous paper on this species (9) was published before the refinements of the IAM approach were developed. In that paper, 391 rotational spectral lines measured by ourselves and other investigators ($5, 14$) were fit to an rms deviation of 1.2 MHz. It is of interest to determine whether an improved fit can be obtained with the same extended treatment that was successful for methanol and methanol-13. In this paper, we report the results of the extended treatment, which show that the rotational spectrum of CH_3OD can indeed be fit to the accuracy of high-resolution experimental measurements.

II. THEORY

The extended IAM treatment utilized has been discussed in detail previously (2–$5, 8$). Briefly, the torsional–rotational Hamiltonian is subjected to a series of coordinate transformations to eliminate the lowest order interaction term between end-over-end rigid body rotational motion and torsion (internal motion). Higher-order interaction terms are, however, necessary to analyze the spectrum to the accuracy obtainable in our high-resolution millimeter-wave and submillimeter-wave experiments (50–100 kHz). The latest Hamiltonian developed here contains high-order centrifugal distortion terms of the A-reduced Watson Hamiltonian in addition to high-order interaction terms, as shown in matrix form in Ref. (4).

The Hamiltonian is diagonalized seriatim. With 21 one-dimensional free rotor basis functions of A and E symmetry, respectively, the torsional Hamiltonian is diagonalized separately to determine torsional eigenvalues and eigenfunctions for the A and E symmetry levels. The symmetry designations arise from the point group symmetry of the methyl group (C_3) which is considered to undergo the internal rotation. The torsional levels so determined are characterized by a pseudo-vibrational quantum number $v_t = 0, 1, 2, \ldots$ in addition to the symmetry specification. The torsional eigenfunctions are then multiplied by prolate symmetric top basis functions to form a product basis for diagonalization of the entire Hamiltonian. The torsional and total diagonalizations must be repeated for each value of the prolate quantum number K desired, because the coordinate transformations utilized to eliminate the rotational–torsional interaction to the lowest order have the effect of adding a K dependence to the transformed torsional portion of the Hamiltonian.

The torsional–rotational eigenvalues and eigenfunctions obtained by the diagonalization can be utilized to determine spectroscopic frequencies and intensities as functions of the spectroscopic parameters in the Hamiltonian. In low-lying torsional states, the rotational spectra of the A symmetry sublevels bear a close resemblance to the spectrum of a quasi-rigid asymmetric top near the prolate limit, whereas the rotational spectra of the E symmetry levels have little in common with that of an asymmetric top. The rotational levels in both states are not characterized by the standard J, K_a, K_c asymmetric top description. Rather, for the A levels, the levels are designated by

the J and K (prolate) quantum numbers ($K \geq 0$), plus a parity ($\pm$) designation, which refers only to the adding and subtracting of $|J, K\rangle$ and $|J, -K\rangle$ basis functions (5). For the E levels, the J, K description, where $-J \leq K \leq J$, is sufficient to define the energy levels. Use of an asymmetric top description is feasible for the rotational levels in the A torsional substates.

Methanol has nonzero dipole components along its a and b axes. The correct values for these along the internal axes in the case of CH_3OD have been measured by Kaushik et al. (14) to be $\mu_a = 0.833$ D and $\mu_b = 1.488$ D. The selection rules for strong rotational transitions in the A states are $\Delta J = 0$; $\Delta K = 0, \pm 1$; $+ \leftrightarrow -$ and $\Delta J = \pm 1$; $\Delta K = 0, \pm 1$, $+ \leftrightarrow +$, $- \leftrightarrow -$. For the E states, the selection rules for strong transitions are $\Delta J = 0, \pm 1$, $\Delta K = 0, \pm 1$. Use of the description "b-type transitions" for $\Delta K = \pm 1$ transitions in the E states is not advisable since these can be "b-type" or "c-type" in the asymmetric top sense. Intensities must be calculated by including the effects of the torsional wave functions. The calculation of intensities here for rotational transitions contains the model assumption that torsion is a one-dimensional motion in which as the methyl rotates, all other bond distances and angles remain fixed. This assumption is only approximately true; work on the internal rotors HSSH (15) and acetaldehyde (16) shows that significant other structural changes can occur during internal rotation. These effects will lead to effective nonzero derivatives with respect to torsional angle for the dipole components, not present in the one-dimensional treatment. The size of the derivatives is expected to be such that they will not change the intensities of the rotational transitions greatly. For transitions in which torsional quantum number changes, however, the dipole derivatives may play a more decisive role in both intensities and selection rules.

III. ANALYSIS AND DISCUSSION

The transitions analyzed here are listed in Tables I (A torsional levels) and II (E torsional levels). These tables contain assigned quantum numbers, frequencies, residuals (observed–calculated), upper and lower state wavenumbers, and intensities. The wavenumbers are listed with respect to the zero-point wavenumber of the $v_t = 0$ A torsional sublevel. The intensities are reported in the form of the component of the dipole moment squared (D^2) multiplied by the S value (17). Much of the data in these tables has been measured previously by ourselves and other investigators ($5, 9, 14$). The additional lines not contained in our previous paper, many of which belong to the first two excited torsional states, have been studied via our standard spectroscopic techniques (18). In a procedure analogous to that used for $^{12}CH_3OH$ and $^{13}CH_3OH$, a variety of transitions were removed from the current data set (19) because they failed loop tests, were poorly determined blends, or because they deviated from "error curves," which are smooth plots of residuals versus quantum numbers for related groups of transitions. The lines in both tables are composed of transitions from the three lowest torsional states ($v_t = 0, 1, 2$) although the great majority of lines are from the lowest torsional state. The highest angular momentum quantum number of the assigned transitions is $J = 9$.

To fit the 226 lines reported for the A torsional states requires varying 32 spectroscopic parameters, whereas to fit the 246 lines reported for the E torsional states requires varying 42 spectroscopic parameters. The values of these parameters and their uncertainties (1σ) are listed in Table III. These parameters comprise rotational constants, A-reduced centrifugal distortion constants, and interaction constants multiplying mixed torsional–rigid body rotational angular momentum expressions in the overall

TABLE I

CH₃OD A Transitions

v_t	J'	K'	P'	J"	K"	P"	Frequency (MHz)	Residual (MHz)	E_U (cm⁻¹)	E_L (cm⁻¹)	μ^2S
0	3	1	−	3	1	+	8160.97	−0.01	13.66	13.39	0.40
0	9	2	+	8	3	+	10279.78	−0.03	83.31	82.97	2.44
0	4	1	−	4	1	+	13600.16	0.02	19.80	19.35	0.30
0	7	1	−	6	2	−	15467.91	0.08	47.43	46.91	2.42
0	8	1	+	7	2	+	15720.99	−0.07	58.07	57.54	2.41
0	5	1	−	5	1	+	20396.67	0.02	27.48	26.79	0.24
0	6	2	+	7	1	+	23407.52	0.05	46.94	46.16	2.04
0	6	1	−	6	1	+	28547.81	0.05	36.68	35.73	0.20
0	5	2	−	6	1	−	34537.29	−0.13	37.84	36.68	1.85
0	7	1	−	7	1	+	38049.06	−0.01	47.43	46.16	0.16
0	7	3	−	8	2	−	38510.10	0.06	70.87	69.58	1.95
2	1	0	+	0	0	+	45193.74	0.08	293.40	291.89	0.70
1	1	0	+	0	0	+	45266.32	0.02	217.56	216.05	0.69
0	1	0	+	0	0	+	45359.40	0.04	1.51	0.00	0.71
0	8	1	−	8	1	+	48894.00	0.10	59.70	58.07	0.14
0	4	0	+	3	1	+	52098.82	0.04	15.12	13.39	3.32
0	5	2	+	6	1	+	63498.66	−0.02	37.85	35.73	1.63
0	8	1	−	7	2	−	66100.09	0.05	59.70	57.49	3.01
0	6	3	+	7	2	+	82040.93	0.03	60.28	57.54	1.49
0	6	3	−	7	2	−	83534.60	0.05	60.28	57.49	1.49
0	4	2	−	5	1	−	83903.30	−0.04	30.27	27.48	1.31
0	2	1	+	1	1	+	89355.10	0.01	8.92	5.94	1.07
2	2	1	+	1	1	+	89707.75	0.16	345.79	342.80	1.05
1	2	1	+	1	1	+	89961.38	−0.09	199.63	196.63	1.00
2	2	0	+	1	0	+	90386.36	0.11	296.41	293.40	1.39
0	2	0	+	1	0	+	90705.81	0.01	4.54	1.51	1.42
1	2	1	−	1	1	−	91120.76	0.01	199.69	196.65	1.00
0	2	1	−	1	1	−	92075.51	−0.04	9.05	5.98	1.07
0	1	1	−	1	0	+	133925.42	−0.23	5.98	1.51	3.18
0	3	1	+	2	1	+	134021.28	0.06	13.39	8.92	1.90
2	3	1	+	2	1	+	134559.30	−0.11	350.28	345.79	1.86
1	3	1	+	2	1	+	134925.71	−0.01	204.13	199.63	1.78
0	2	1	−	2	0	+	135295.24	−0.17	9.05	4.54	5.27
2	3	2	−	2	2	−	135526.27	0.03	446.11	441.59	1.15
2	3	2	+	2	2	+	135528.03	0.03	446.11	441.59	1.15
2	3	0	+	2	0	+	135576.81	0.08	300.94	296.41	2.09
1	3	2	+	2	2	+	135652.68	0.00	194.82	190.30	1.22
1	3	2	−	2	2	−	135663.66	−0.04	194.82	190.30	1.22
1	3	0	+	2	0	+	135806.80	−0.10	225.11	220.58	2.07
0	3	0	+	2	0	+	136026.40	0.01	9.08	4.54	2.13
0	3	2	−	2	2	−	136055.46	−0.05	24.22	19.69	1.21
0	3	2	+	2	2	+	136102.82	0.02	24.23	19.69	1.21
2	3	1	−	2	1	−	136593.95	0.04	350.42	345.86	1.86
1	3	1	−	2	1	−	136663.96	0.00	204.25	199.69	1.79
0	3	1	−	3	0	+	137370.45	−0.02	13.66	9.08	7.32
0	3	1	−	2	1	−	138101.53	0.08	13.66	9.05	1.91
0	4	1	−	4	0	+	140175.20	0.03	19.80	15.12	9.30
0	5	1	−	5	0	+	143741.65	0.06	27.48	22.68	11.20
0	6	1	−	6	0	+	148109.25	0.12	36.68	31.74	12.99
0	6	0	+	5	1	+	148359.77	−0.25	31.74	26.79	5.74
0	7	1	−	7	0	+	153324.00	0.16	47.43	42.31	14.67
0	8	1	−	8	0	+	159437.46	0.02	59.70	54.38	16.21
0	9	1	−	9	0	+	166505.74	−0.24	73.50	67.95	17.60
0	4	1	+	3	1	+	178673.89	0.08	19.35	13.39	2.68
2	4	1	+	3	1	+	179408.81	−0.02	356.26	350.28	2.61
1	4	1	+	3	1	+	179870.33	−0.01	210.13	204.13	2.51
2	4	2	−	3	2	−	180697.27	0.08	452.14	446.11	2.07
2	4	2	+	3	2	+	180701.61	0.04	452.14	446.11	2.07
2	4	0	+	3	0	+	180764.11	0.08	306.97	300.94	2.78
1	4	2	+	3	2	+	180847.81	0.00	200.85	194.82	2.19
1	4	2	−	3	2	−	180875.29	0.00	200.86	194.82	2.19
1	4	0	+	3	0	+	181085.17	−0.07	231.15	225.11	2.76
0	4	0	+	3	0	+	181308.20	−0.07	15.12	9.08	2.84
0	4	2	−	3	2	−	181388.97	0.04	30.27	24.22	2.17
0	4	2	+	3	2	+	181507.14	0.02	30.28	24.23	2.17
2	4	1	−	3	1	−	182120.91	0.01	356.49	350.42	2.61
1	4	1	−	3	1	−	182186.48	0.00	210.32	204.25	2.51
0	7	0	+	6	1	+	197233.48	−0.23	42.31	35.73	7.03
0	2	1	+	1	0	+	221920.25	−0.20	8.92	1.51	3.18
0	5	1	+	4	1	+	223308.57	0.01	26.79	19.35	3.43
2	5	1	+	4	1	+	224255.06	−0.02	363.74	356.26	3.35
1	5	1	+	4	1	+	224789.07	−0.02	217.63	210.13	3.22
2	5	2	−	4	2	−	225864.35	0.05	459.67	452.14	2.90
2	5	2	+	4	2	+	225873.05	−0.02	459.67	452.14	2.90
2	5	0	+	4	0	+	225947.17	0.10	314.50	306.97	3.48
1	5	2	+	4	2	+	226023.71	−0.02	208.39	200.85	3.06
1	5	4	+	4	4	+	226030.50	0.13	281.80	274.26	1.37
1	5	4	−	4	4	−	226030.50	0.13	281.80	274.26	1.37
1	5	2	−	4	2	−	226078.57	−0.01	208.40	200.86	3.06
1	5	3	+	4	3	+	226331.80	−0.01	233.27	225.72	2.24
1	5	3	−	4	3	−	226334.09	−0.03	233.27	225.72	2.24
1	5	0	+	4	0	+	226371.54	−0.07	238.70	231.15	3.45
0	5	0	+	4	0	+	226538.67	0.03	22.68	15.12	3.55
0	5	2	−	4	2	−	226706.60	0.02	37.84	30.27	3.04
0	5	3	−	4	3	−	226778.74	0.11	51.20	43.64	2.31
0	5	2	+	4	2	+	226942.83	0.06	37.85	30.28	3.04

TABLE I—*Continued*

v_t	J'	K'	P'	J"	K"	P"	Frequency (MHz)	Residual (MHz)	E_U (cm^{-1})	E_L (cm^{-1})	$\mu^2 S$
2	5	1	−	4	1	−	227644.20	0.01	364.08	356.49	3.35
1	5	1	−	4	1	−	227681.29	0.01	217.92	210.32	3.22
0	5	1	−	4	1	−	230105.10	0.03	27.48	19.80	3.43
0	3	1	+	2	0	+	265235.85	−0.03	13.39	4.54	4.26
0	6	1	+	5	1	+	267921.47	0.08	35.73	26.79	4.16
2	6	1	+	5	1	+	269097.34	−0.01	372.72	363.74	4.07
1	6	1	+	5	1	+	269676.03	0.03	226.62	217.63	3.91
2	6	2	−	5	2	−	271026.68	0.05	468.71	459.67	3.69
2	6	2	+	5	2	+	271041.88	−0.07	468.71	459.67	3.69
2	6	0	+	5	0	+	271124.91	0.06	323.55	314.50	4.17
1	6	2	+	5	2	+	271175.72	0.01	217.44	208.39	3.89
1	6	4	−	5	4	−	271223.09	−0.09	290.85	281.80	2.55
1	6	4	+	5	4	+	271223.09	−0.10	290.85	281.80	2.55
1	6	2	−	5	2	−	271271.34	−0.04	217.45	208.40	3.89
1	6	3	+	5	3	+	271633.59	−0.02	242.34	233.27	3.15
1	6	3	−	5	3	−	271639.71	−0.05	242.34	233.27	3.15
1	6	0	+	5	0	+	271668.04	−0.01	247.76	238.70	4.14
0	6	0	+	5	0	+	271704.93	−0.04	31.74	22.68	4.26
0	6	2	−	5	2	−	272004.51	−0.03	46.91	37.84	3.86
0	6	5	−	5	5	−	272094.81	−0.03	105.53	96.45	0.98
0	6	5	+	5	5	+	272094.81	−0.03	105.53	96.45	0.98
0	6	3	−	5	3	−	272138.32	−0.02	60.28	51.20	3.25
0	6	2	+	5	2	+	272417.28	0.02	46.94	37.85	3.86
1	6	1	−	5	1	−	273141.10	−0.11	227.03	217.92	3.92
2	6	1	−	5	1	−	273162.83	−0.03	373.20	364.08	4.07
0	6	1	−	5	1	−	276072.52	0.02	36.68	27.48	4.17
0	9	2	+	9	1	−	294266.75	0.05	83.31	73.50	11.44
0	9	0	+	8	1	+	296158.27	0.14	67.95	58.07	9.83
0	8	2	+	8	1	−	298895.68	0.05	69.67	59.70	9.88
0	7	2	+	7	1	−	303296.12	0.00	57.54	47.43	8.41
0	6	2	+	6	1	−	307368.18	0.00	46.94	36.68	7.02
0	4	1	+	3	0	+	307883.55	0.25	19.35	9.08	5.35
0	5	2	+	5	1	−	311023.41	−0.01	37.85	27.48	5.69
0	7	1	+	6	1	+	312508.44	−0.03	46.16	35.73	4.89
2	7	1	+	6	1	+	313934.89	0.02	383.19	372.72	4.78
0	4	2	+	4	1	+	314185.68	−0.05	30.28	19.80	4.41
1	7	1	+	6	1	+	314525.44	0.03	237.12	226.62	4.60
2	7	2	−	6	2	−	316183.26	0.06	479.26	468.71	4.44
2	7	2	+	6	2	+	316207.57	−0.11	479.26	468.71	4.44
2	7	0	+	6	0	+	316296.32	0.03	334.10	323.55	4.87
1	7	2	+	6	2	+	316299.05	0.03	227.99	217.44	4.68
1	7	4	−	6	4	−	316408.50	−0.08	301.40	290.85	3.60
1	7	4	+	6	4	+	316408.50	−0.09	301.40	290.85	3.60
1	7	2	−	6	2	−	316451.49	0.00	228.00	217.45	4.68
0	3	2	+	3	1	+	316791.59	0.02	24.23	13.66	3.12
0	7	0	+	6	0	+	316795.07	0.00	42.31	31.74	4.97
1	7	3	+	6	3	+	316953.46	0.04	252.91	242.34	4.00
1	7	3	−	6	3	−	316967.22	−0.03	252.91	242.34	4.00
1	7	0	+	6	0	+	316976.56	0.01	258.33	247.76	4.83
0	7	2	−	6	2	−	317278.87	0.00	57.49	46.91	4.66
0	7	5	+	6	5	+	317438.88	0.00	116.12	105.53	2.09
0	7	5	−	6	5	−	317438.88	0.00	116.12	105.53	2.09
0	7	3	−	6	3	−	317501.18	0.00	70.87	60.28	4.13
0	7	2	+	6	2	+	317937.73	0.01	57.54	46.94	4.66
1	7	1	−	6	1	−	318559.06	0.04	237.66	227.03	4.61
2	7	1	−	6	1	−	318675.90	−0.07	383.83	373.20	4.78
0	2	2	+	2	1	+	318790.25	0.03	19.69	9.05	1.76
0	7	1	−	6	1	−	322009.76	−0.02	47.43	36.68	4.90
0	2	2	−	2	1	+	322859.20	0.05	19.69	8.92	1.73
0	3	2	−	3	1	+	324893.49	0.07	24.22	13.39	3.02
0	4	2	−	4	1	+	327608.56	0.01	30.27	19.35	4.16
0	5	2	−	5	1	+	331006.54	−0.03	37.84	26.79	5.23
0	6	2	−	6	1	+	335089.66	−0.05	46.91	35.73	6.24
0	7	2	−	7	1	+	339860.10	−0.01	57.49	46.16	7.20
0	8	2	−	8	1	+	345319.59	0.04	69.58	58.07	8.11
0	5	1	+	4	0	+	349883.62	0.03	26.79	15.12	6.48
0	9	2	−	9	1	+	351469.26	0.07	83.19	71.46	8.98
0	8	1	+	7	1	+	357066.22	−0.04	58.07	46.16	5.61
2	8	1	+	7	1	+	358766.87	0.02	395.16	383.19	5.49
1	8	1	+	7	1	+	359332.15	−0.01	249.10	237.12	5.29
2	8	2	−	7	2	−	361333.10	0.05	491.31	479.26	5.18
2	8	2	+	7	2	+	361369.62	−0.09	491.31	479.26	5.18
1	8	2	+	7	2	+	361389.06	0.05	240.04	227.99	5.46
2	8	0	+	7	0	+	361460.21	−0.14	346.15	334.10	5.56
1	8	4	+	7	4	+	361585.25	0.04	313.46	301.40	4.58
1	8	4	−	7	4	−	361585.25	0.08	313.46	301.40	4.58
1	8	2	−	7	2	−	361616.67	−0.03	240.06	228.00	5.46
0	8	0	+	7	0	+	361797.57	0.10	54.38	42.31	5.67
1	8	3	+	7	3	+	362293.12	−0.01	264.99	252.91	4.81
1	8	0	+	7	0	+	362299.21	0.11	270.42	258.33	5.52
1	8	3	−	7	3	−	362320.73	0.07	264.99	252.91	4.81
0	8	2	−	7	2	−	362525.70	0.00	69.58	57.49	5.43
0	8	5	−	7	5	−	362780.48	−0.06	128.22	116.12	3.48
0	8	5	+	7	5	+	362780.48	−0.05	128.22	116.12	3.48
0	8	3	+	7	3	+	362842.70	−0.12	82.97	70.87	4.97
0	8	4	−	7	4	−	362845.11	0.25	101.27	89.17	4.28
0	8	4	+	7	4	+	362845.11	−0.03	101.27	89.17	4.28
0	8	3	−	7	3	−	362868.49	0.01	82.97	70.87	4.97

TABLE I—*Continued*

v_t	J'	K'	P'	J"	K"	P"	Frequency (MHz)	Residual (MHz)	E_U (cm^{-1})	E_L (cm^{-1})	$\mu^2 S$
0	8	2	+	7	2	+	363510.60	0.01	69.67	57.54	5.43
1	8	1	−	7	1	−	363927.43	0.05	249.80	237.66	5.31
2	8	1	−	7	1	−	364182.64	0.06	395.97	383.83	5.49
0	8	1	−	7	1	−	367911.01	−0.07	59.70	47.43	5.62
0	6	1	+	5	0	+	391266.37	0.04	35.73	22.68	7.64
0	9	3	−	9	2	+	398009.24	0.00	96.59	83.31	9.41
0	8	3	−	8	2	+	398908.53	−0.02	82.97	69.67	8.22
0	7	3	−	7	2	+	399550.61	−0.04	70.87	57.54	7.04
0	6	3	−	6	2	+	399987.14	−0.05	60.28	46.94	5.84
0	5	3	−	5	2	+	400266.10	−0.02	51.20	37.85	4.60
0	4	3	−	4	2	+	400430.21	−0.04	43.64	30.28	3.28
0	3	3	−	3	2	+	400516.34	0.01	37.59	24.23	1.82
0	3	3	+	3	2	−	400575.32	−0.03	37.59	24.22	1.82
0	4	3	+	4	2	−	400606.86	0.01	43.64	30.27	3.28
0	5	3	+	5	2	−	400676.74	−0.02	51.20	37.84	4.59
0	6	3	+	6	2	−	400804.82	−0.03	60.28	46.91	5.83
0	7	3	+	7	2	−	401014.29	−0.03	70.87	57.49	7.02
0	8	3	+	8	2	−	401331.42	−0.02	82.97	69.58	8.18
0	9	1	+	8	1	+	401591.44	−0.05	71.46	58.07	6.33
0	9	3	+	9	2	−	401785.24	−0.01	96.59	83.19	9.33
0	9	0	+	8	0	+	406701.87	0.19	67.95	54.38	6.38
0	9	2	−	8	2	−	407741.13	0.00	83.19	69.58	6.19
0	9	5	+	8	5	+	408119.47	0.07	141.83	128.22	4.45
0	9	5	−	8	5	−	408119.47	0.06	141.83	128.22	4.45
0	9	3	−	8	3	−	408241.94	−0.02	96.59	82.97	5.79
0	9	2	+	8	2	+	409141.21	−0.07	83.31	69.67	6.19
0	2	2	−	1	1	−	410854.05	0.11	19.69	5.98	3.12
0	2	2	+	1	1	+	412226.18	0.11	19.69	5.94	3.10
0	7	1	+	6	0	+	432070.13	0.29	46.16	31.74	8.86
0	3	2	−	2	1	−	454833.78	−0.12	24.22	9.05	3.47
0	3	2	+	2	1	+	458973.83	0.05	24.23	8.92	3.40
0	8	1	+	7	0	+	472341.09	0.06	58.07	42.31	10.13
0	4	2	−	3	1	−	498121.39	0.02	30.27	13.66	3.91
0	4	2	+	3	1	+	506459.69	0.02	30.28	13.39	3.77
0	9	1	+	8	0	+	512134.79	−0.25	71.46	54.38	11.47
0	3	3	−	2	2	+	536618.98	−0.05	37.59	19.69	5.15
0	5	2	−	4	1	−	540714.93	−0.06	37.84	19.80	4.39
0	9	4	+	9	3	−	548581.99	−0.21	114.89	96.59	8.84
0	8	4	+	8	3	−	548622.41	0.27	101.27	82.97	7.58
0	7	4	+	7	3	−	548645.59	0.11	89.17	70.87	6.29
0	6	4	+	6	3	−	548657.81	−0.18	78.58	60.28	4.94
0	5	2	+	4	1	+	554728.60	−0.04	37.85	19.35	4.13
0	4	3	+	3	2	+	581936.70	0.04	43.64	24.23	5.39
0	6	2	+	5	1	+	603837.34	0.00	46.94	26.79	4.47
0	7	2	−	6	1	−	623820.80	−0.02	57.49	36.68	5.45
0	5	3	+	4	2	+	627206.16	0.13	51.20	30.28	5.72
0	5	3	−	4	2	−	627386.15	−0.05	51.20	30.27	5.72
0	7	2	+	6	1	+	653853.57	−0.10	57.54	35.73	4.78
0	8	2	−	7	1	−	664336.71	−0.02	69.58	47.43	6.01
0	6	3	−	5	2	−	672817.98	0.03	60.28	37.84	6.10
0	9	2	−	8	1	−	704166.88	0.09	83.19	59.70	6.61
0	8	2	+	7	1	+	704855.72	−0.06	69.67	46.16	5.04

Hamiltonian. The interaction constants are defined in Ref. (*4*). Despite the large number of parameters needed, especially for the *E* state data, there are still substantial redundancies in the two fits. The rms deviations obtained are 81 kHz for the *A* species and 92 kHz for the *E* species. The size of these deviations are of the order of our experimental uncertainties (50–100 kHz) so that we have succeeded in fitting the spectral transitions in Tables I and II to experimental accuracy. In addition, the spectroscopic parameters shown in Table III can be used to predict the frequencies and intensities of a large number of transitions not measured in the laboratory through *J* = 12. These predictions are available upon request.

The spectroscopic constants obtained from this work are listed in Table III along with a smaller set of constants obtained in our previous fit to a global data set consisting of 391 transitions from torsional levels of both *A* and *E* symmetry. The 20 spectroscopic constants previously determined (*9*) contain only a few low-order distortion and interaction parameters, among which are two so-called Kirtman interaction constants $-k_1$ and k_2 (*20*). With the present data set, k_1 and k_2 cannot be determined in our current separate fits to the *A* and *E* state data; therefore, they have been fixed at their

TABLE II

CH$_3$OD E Transitions

v_t	J'	K'	J"	K"	Frequency (MHz)	Residual (MHz)	E_U (cm^{-1})	E_L (cm^{-1})	μ^2S
0	3	2	4	1	14920.43	-0.04	20.56	20.07	0.78
0	9	-1	9	0	15948.14	-0.02	69.64	69.11	2.96
0	8	-1	8	0	17056.86	-0.03	56.14	55.57	3.44
0	7	-1	7	0	17888.64	-0.09	44.12	43.52	3.79
0	6	-1	6	0	18454.76	0.07	33.59	32.97	3.96
0	5	-1	5	0	18792.97	0.12	24.54	23.92	3.91
0	4	-1	4	0	18957.17	0.05	17.00	16.37	3.62
0	1	-1	1	0	18957.95	0.03	3.39	2.76	1.48
0	2	-1	2	0	18991.67	0.00	6.42	5.79	2.37
0	3	-1	3	0	19005.64	0.01	10.96	10.32	3.09
0	3	0	2	1	25695.84	-0.04	10.32	9.46	1.02
0	5	1	4	2	30839.20	-0.04	27.65	26.62	1.24
0	7	3	8	2	39246.81	-0.01	67.30	65.99	1.93
0	4	-2	5	-1	43658.76	0.01	26.00	24.54	1.20
0	7	-1	6	-2	43945.92	0.03	44.12	42.65	1.95
2	1	0	0	0	45190.13	-0.06	372.56	371.05	0.69
1	1	0	0	0	45260.02	0.10	179.81	178.30	0.68
0	1	0	0	0	45344.16	-0.06	2.76	1.25	0.76
0	2	2	3	1	60487.65	-0.20	16.02	14.01	0.35
0	1	-1	0	0	64302.16	0.02	3.39	1.25	1.02
0	4	0	3	1	70715.45	-0.07	16.37	14.01	1.49
0	2	0	1	-1	71711.91	-0.06	5.79	3.39	0.53
0	6	1	5	2	76868.83	-0.11	36.75	34.19	1.69
0	6	3	7	2	85003.12	-0.06	56.71	53.87	1.49
0	8	-1	7	-2	86510.22	-0.02	56.14	53.25	2.20
0	3	-2	4	-1	88340.24	0.00	19.94	17.00	0.77
2	2	1	1	1	90368.97	0.02	418.13	415.11	1.04
2	2	-1	1	-1	90381.26	0.10	306.95	303.93	1.05
0	2	0	1	0	90669.98	0.09	5.79	2.76	1.52
0	2	-1	1	-1	90703.65	0.01	6.42	3.39	1.08
0	2	1	1	1	90743.56	-0.02	9.46	6.44	1.09
0	1	1	1	0	110188.86	-0.02	6.44	2.76	1.57
0	2	1	2	0	110262.64	0.07	9.46	5.79	2.66
0	3	1	3	0	110475.76	-0.05	14.01	10.32	3.82
0	4	1	4	0	110950.75	0.04	20.07	16.37	5.06
0	5	1	5	0	111846.30	0.06	27.65	23.92	6.37
0	7	1	7	0	115674.45	0.11	47.38	43.52	9.15
0	8	1	8	0	119025.80	-0.01	59.54	55.57	10.52
2	3	1	2	1	135551.99	0.06	422.65	418.13	1.84
2	3	-2	2	-2	135586.91	-0.06	327.52	323.00	1.16
2	3	2	2	2	135628.15	0.10	345.96	341.44	1.13
1	3	1	2	1	135721.43	-0.11	183.92	179.39	1.87
1	3	0	2	0	135760.13	-0.09	187.35	182.82	2.05
1	3	-1	2	-1	135760.13	-0.01	218.49	213.96	1.92
1	3	2	2	2	135764.74	-0.06	214.14	209.61	1.17
1	3	-2	2	-2	135894.21	-0.16	223.10	218.57	1.06
0	3	0	2	0	135958.38	-0.06	10.32	5.79	2.28
0	3	-1	2	-1	135972.50	0.10	10.96	6.42	1.91
0	3	2	2	2	136098.96	0.11	20.56	16.02	1.20
0	3	-2	2	-2	136107.60	-0.02	19.94	15.40	1.19
0	3	1	2	1	136171.61	-0.07	14.01	9.46	1.93
0	7	-3	8	-2	143472.33	-0.13	70.16	65.37	1.94
0	3	-1	2	0	154963.98	-0.09	10.96	5.79	2.20
0	1	1	0	0	155533.08	-0.02	6.44	1.25	1.02
0	6	0	5	1	159571.09	0.01	32.97	27.65	2.22
0	4	0	3	-1	162185.73	0.04	16.37	10.96	1.77
2	4	3	3	3	180674.12	-0.11	331.10	325.07	1.26
2	4	-3	3	-3	180712.50	0.24	424.76	418.73	1.21
2	4	1	3	1	180733.15	0.00	428.68	422.65	2.59
2	4	-1	3	-1	180754.10	-0.08	317.50	311.47	2.64
2	4	0	3	0	180756.29	-0.37	386.13	380.10	2.77
2	4	-2	3	-2	180776.26	-0.05	333.55	327.52	2.09
2	4	2	3	2	180831.79	0.10	351.99	345.96	2.03
1	4	1	3	1	180944.09	-0.14	189.95	183.92	2.63
1	4	0	3	0	180990.81	-0.04	193.39	187.35	2.74
1	4	2	3	2	181024.15	0.10	220.18	214.14	2.10
1	4	-1	3	-1	181030.70	-0.04	224.53	218.49	2.70
1	4	-2	3	-2	181126.29	-0.11	229.15	223.10	1.92
0	4	-1	3	-1	181142.85	0.04	17.00	10.96	2.69
0	4	0	3	0	181191.27	-0.05	16.37	10.32	3.04
0	4	-3	3	-3	181428.24	0.07	42.92	36.87	1.26
0	4	3	3	3	181451.29	0.03	40.06	34.01	1.25
0	4	2	3	2	181486.11	0.10	26.62	20.56	2.16
0	4	-2	3	-2	181504.50	0.06	26.00	19.94	2.14
0	4	1	3	1	181666.31	0.09	20.07	14.01	2.71
0	6	-3	7	-2	189221.75	-0.19	59.57	53.25	1.49
0	9	2	9	1	191870.15	-0.11	79.63	73.23	11.05
0	8	2	8	1	193358.93	0.05	65.99	59.54	9.43
0	7	2	7	1	194568.61	0.17	53.87	47.38	8.02
0	5	2	5	1	196053.73	0.09	34.19	27.65	5.51
0	4	2	4	1	196406.57	0.09	26.62	20.07	4.30
0	3	2	3	1	196586.65	-0.05	20.56	14.01	3.08
0	2	2	2	1	196659.35	-0.18	16.02	9.46	1.75
0	2	1	1	0	200932.39	-0.07	9.46	2.76	1.48
0	7	0	6	1	203024.71	0.02	43.52	36.75	2.44

TABLE II—*Continued*

v_t	J'	K'	J"	K"	Frequency (MHz)	Residual (MHz)	E_U (cm⁻¹)	E_L (cm⁻¹)	$\mu^2 S$
0	5	0	4	-1	207393.09	0.01	23.92	17.00	2.55
1	5	4	4	4	225300.08	-0.11	254.30	246.78	1.72
2	5	-4	4	-4	225832.19	0.04	466.00	458.47	1.21
2	5	3	4	3	225834.64	-0.11	338.63	331.10	2.31
2	5	-3	4	-3	225885.42	0.19	432.30	424.76	2.21
2	5	4	4	4	225911.36	-0.15	415.61	408.07	1.25
2	5	1	4	1	225912.05	0.06	436.21	428.68	3.32
2	5	-1	4	-1	225935.08	-0.01	325.03	317.50	3.37
2	5	0	4	0	225942.39	-0.35	393.66	386.13	3.47
2	5	-2	4	-2	225960.29	0.06	341.09	333.55	2.92
2	5	2	4	2	226030.50	0.03	359.53	351.99	2.84
1	5	1	4	1	226151.52	-0.10	197.50	189.95	3.37
0	5	-1	4	-1	226185.93	0.00	24.54	17.00	3.44
1	5	0	4	0	226201.95	-0.04	200.94	193.39	3.42
1	5	2	4	2	226287.06	0.06	227.72	220.18	2.94
1	5	-2	4	-2	226302.28	0.05	236.69	229.15	2.70
1	5	-1	4	-1	226315.85	-0.08	232.08	224.53	3.46
0	5	0	4	0	226350.19	0.00	23.92	16.37	3.80
0	5	-4	4	-4	226738.86	-0.10	71.15	63.58	1.31
0	5	4	4	4	226769.54	0.16	69.87	62.31	1.29
0	5	-3	4	-3	226788.61	-0.06	50.49	42.92	2.31
0	5	3	4	3	226825.54	0.11	47.63	40.06	2.28
0	5	2	4	2	226892.86	-0.03	34.19	26.62	3.02
0	5	-2	4	-2	226922.58	-0.01	33.57	26.00	3.00
0	5	1	4	1	227245.71	-0.01	27.65	20.07	3.47
0	5	-3	6	-2	234886.65	0.00	50.49	42.65	1.05
0	5	-1	4	0	245142.99	-0.06	24.54	16.37	3.77
0	8	0	7	1	245538.04	0.01	55.57	47.38	2.55
0	3	1	2	0	246434.17	-0.09	14.01	5.79	1.89
0	6	0	5	-1	252624.44	-0.03	32.97	24.54	3.48
0	2	-2	2	-1	269347.82	-0.01	15.40	6.42	1.79
0	3	-2	3	-1	269483.06	0.02	19.94	10.96	3.14
0	4	-2	4	-1	269844.68	0.00	26.00	17.00	4.37
1	6	4	5	4	270373.22	0.04	263.32	254.30	3.16
0	5	-2	5	-1	270581.39	0.04	33.57	24.54	5.55
2	6	3	5	3	270989.88	-0.02	347.67	338.63	3.25
2	6	-4	5	-4	270991.36	0.03	475.04	466.00	2.24
2	6	-3	5	-3	271054.92	0.12	441.34	432.30	3.10
0	6	-1	5	-1	271079.19	0.03	33.59	24.54	4.18
2	6	1	5	1	271087.99	0.11	445.26	436.21	4.03
2	6	-1	5	-1	271110.94	0.02	334.08	325.03	4.10
2	6	0	5	0	271126.54	-0.22	402.71	393.66	4.16
2	6	-2	5	-2	271137.40	0.01	350.13	341.09	3.71
2	6	2	5	2	271223.09	-0.06	368.58	359.53	3.60
1	6	1	5	1	271339.88	-0.05	206.55	197.50	4.09
1	6	0	5	0	271388.81	0.01	209.99	200.94	4.11
1	6	-2	5	-2	271408.93	0.16	245.75	236.69	3.44
0	6	0	5	0	271417.35	0.03	32.97	23.92	4.56
1	6	2	5	2	271554.57	0.05	236.78	227.72	3.74
1	6	-1	5	-1	271619.08	-0.02	241.14	232.08	4.21
0	6	-2	6	-1	271864.38	0.04	42.65	33.59	6.68
0	6	-4	5	-4	272080.64	-0.01	80.22	71.15	2.42
0	6	4	5	4	272123.15	0.09	78.95	69.87	2.40
0	6	-3	5	-3	272151.45	-0.01	59.57	50.49	3.24
0	6	3	5	3	272207.13	-0.02	56.71	47.63	3.21
0	6	2	5	2	272328.59	0.00	43.27	34.19	3.83
0	6	-2	5	-2	272362.15	0.00	42.65	33.57	3.80
0	6	1	5	1	272922.59	0.00	36.75	27.65	4.21
0	7	-2	7	-1	273870.29	0.00	53.25	44.12	7.75
0	8	-2	8	-1	276756.29	0.02	65.37	56.14	8.77
0	4	-3	5	-2	280460.40	0.25	42.92	33.57	0.63
0	9	-2	9	-1	280630.77	-0.02	79.00	69.64	9.69
0	6	-1	5	0	289871.93	-0.09	33.59	23.92	4.77
0	4	1	3	0	292141.96	-0.07	20.07	10.32	2.23
0	7	0	6	-1	297921.37	-0.13	43.52	33.59	4.58
1	7	4	6	4	315450.75	0.10	273.84	263.32	4.45
0	7	-1	6	-1	315810.23	0.01	44.12	33.59	4.93
2	7	3	6	3	316138.63	0.01	358.22	347.67	4.13
2	7	-4	6	-4	316146.50	-0.03	485.59	475.04	3.16
2	7	-3	6	-3	316220.25	-0.05	451.89	441.34	3.94
2	7	1	6	1	316260.19	-0.01	455.81	445.26	4.74
2	7	4	6	4	316262.17	-0.07	435.20	424.65	3.28
2	7	-1	6	-1	316280.68	0.02	344.63	334.08	4.82
2	7	-2	6	-2	316306.44	0.01	360.68	350.13	4.47
2	7	0	6	0	316308.36	0.07	413.26	402.71	4.85
0	7	0	6	0	316376.22	0.03	43.52	32.97	5.34
2	7	2	6	2	316408.50	-0.01	379.13	368.58	4.34
1	7	-2	6	-2	316434.45	0.19	256.30	245.75	4.16
1	7	1	6	1	316505.35	0.00	217.11	206.55	4.81
1	7	0	6	0	316546.50	0.03	220.55	209.99	4.79
1	7	2	6	2	316827.43	-0.02	247.35	236.78	4.50
1	7	-1	6	-1	316943.41	0.03	251.71	241.14	4.95
0	7	-4	6	-4	317418.98	-0.01	90.81	80.22	3.43
0	7	4	6	4	317476.69	0.07	89.54	78.95	3.39
0	7	-3	6	-3	317517.03	0.00	70.16	59.57	4.12
0	7	3	6	3	317597.90	-0.01	67.30	56.71	4.08
0	7	2	6	2	317807.82	0.00	53.87	43.27	4.62
0	7	-2	6	-2	317816.19	0.01	53.25	42.65	4.58

TABLE II—*Continued*

v_t	J'	K'	J''	K''	Frequency (MHz)	Residual (MHz)	E_U (cm^{-1})	E_L (cm^{-1})	μ^2S
0	7	1	6	1	318699.04	0.01	47.38	36.75	4.94
0	3	-3	4	-2	325954.61	0.04	36.87	26.00	0.26
0	3	2	2	1	332758.27	-0.11	20.56	9.46	3.41
0	7	-1	6	0	334264.92	0.00	44.12	32.97	5.92
0	5	1	4	0	338196.42	-0.01	27.65	16.37	2.48
0	8	0	7	-1	343323.71	0.07	55.57	44.12	5.88
0	2	-2	1	-1	360051.42	-0.04	15.40	3.39	3.16
0	8	-1	7	-1	360380.55	0.02	56.14	44.12	5.69
1	8	4	7	4	360531.52	-0.05	285.87	273.84	5.62
0	8	0	7	0	361212.37	0.00	55.57	43.52	6.12
2	8	3	7	3	361279.99	0.14	370.27	358.22	4.96
2	8	-4	7	-4	361297.07	-0.01	497.64	485.59	4.02
1	8	-2	7	-2	361368.92	-0.20	268.36	256.30	4.87
2	8	-3	7	-3	361380.73	-0.29	463.94	451.89	4.74
2	8	1	7	1	361428.29	-0.09	467.86	455.81	5.44
2	8	4	7	4	361432.78	0.15	447.26	435.20	4.18
2	8	-1	7	-1	361443.33	0.04	356.68	344.63	5.53
2	8	-2	7	-2	361466.02	0.01	372.74	360.68	5.22
2	8	0	7	0	361487.18	0.25	425.32	413.26	5.55
2	8	2	7	2	361585.25	-0.11	391.20	379.13	5.07
1	8	1	7	1	361644.17	0.09	229.17	217.11	5.52
1	8	0	7	0	361670.36	0.08	232.61	220.55	5.48
1	8	2	7	2	362106.50	-0.06	259.43	247.35	5.25
1	8	-1	7	-1	362291.61	0.07	263.80	251.71	5.70
0	8	-4	7	-4	362753.47	0.01	102.91	90.81	4.36
0	8	4	7	4	362830.00	-0.02	101.64	89.54	4.32
0	8	-3	7	-3	362885.85	0.02	82.26	70.16	4.96
0	8	3	7	3	362999.24	0.00	79.41	67.30	4.91
0	8	-2	7	-2	363266.52	0.01	65.37	53.25	5.34
0	8	2	7	2	363354.21	-0.07	65.99	53.87	5.38
0	8	1	7	1	364563.87	0.03	59.54	47.38	5.67
0	4	2	3	1	378072.68	-0.03	26.62	14.01	3.79
0	8	-1	7	0	378269.25	-0.01	56.14	43.52	7.24
0	6	1	5	0	384768.91	0.08	36.75	23.92	2.62
0	9	0	8	-1	388857.48	-0.04	69.11	56.14	7.36
0	9	3	9	2	401655.54	0.06	93.03	79.63	9.57
0	8	3	8	2	402245.98	-0.08	79.41	65.99	8.47
0	7	3	7	2	402601.02	-0.08	67.30	53.87	7.27
0	6	3	6	2	402810.94	-0.07	56.71	43.27	6.03
0	5	3	5	2	402932.43	-0.02	47.63	34.19	4.74
0	4	3	4	2	402999.95	0.04	40.06	26.62	3.38
0	3	3	3	2	403034.83	0.16	34.01	20.56	1.87
0	9	-1	8	-1	404805.71	0.02	69.64	56.14	6.47
0	3	-2	2	-1	405455.44	-0.01	19.94	6.42	3.47
0	9	0	8	0	405914.39	-0.02	69.11	55.57	6.93
0	9	-4	8	-4	408083.54	0.04	116.52	102.91	5.25
0	9	4	8	4	408183.17	-0.07	115.26	101.64	5.19
0	9	-3	8	-3	408258.45	0.08	95.88	82.26	5.77
0	9	3	8	3	408412.61	0.03	93.03	79.41	5.71
0	9	-2	8	-2	408680.19	-0.01	79.00	65.37	6.09
0	9	2	8	2	409003.04	-0.11	79.63	65.99	6.13
0	9	1	8	1	410491.86	0.07	73.23	59.54	6.39
0	9	-1	8	0	421862.55	-0.03	69.64	55.57	8.71
0	5	2	4	1	423299.46	0.08	34.19	20.07	4.18
0	7	1	6	0	432050.51	-0.02	47.38	32.97	2.67
0	4	-2	3	-1	450987.45	-0.04	26.00	10.96	3.84
0	6	2	5	1	468382.41	0.17	43.27	27.65	4.53
0	8	1	7	0	480238.13	-0.05	59.54	43.52	2.61
0	5	-2	4	-1	496767.29	0.01	33.57	17.00	4.19
0	9	-3	9	-2	505936.55	0.10	95.88	79.00	9.33
0	8	-3	8	-2	506358.30	0.02	82.26	65.37	8.28
0	7	-3	7	-2	506738.89	-0.08	70.16	53.25	7.14
0	6	-3	6	-2	507038.07	-0.04	59.57	42.65	5.93
0	5	-3	5	-2	507248.80	-0.01	50.49	33.57	4.68
0	4	-3	4	-2	507382.76	0.02	42.92	26.00	3.34
0	3	-3	3	-2	507459.04	0.03	36.87	19.94	1.85
0	7	2	6	1	513267.64	0.17	53.87	36.75	4.81
0	9	1	8	0	529517.56	-0.04	73.23	55.57	2.47
0	6	-2	5	-1	542943.61	0.11	42.65	24.54	4.48
0	8	2	7	1	557922.64	-0.09	65.99	47.38	4.95
0	9	2	8	1	602361.86	-0.19	79.63	59.54	4.90
0	8	-2	7	-1	637136.73	-0.08	65.37	44.12	4.70
0	9	-2	8	-1	685436.45	-0.03	79.00	56.14	4.55

previous values. The newly determined rotational and low-order distortion and interaction constants have not changed much from the earlier values, nor have their uncertainties improved dramatically. For example, the threefold potential barrier V_3 of 366.1 cm^{-1} has been superseded by values of 369.3 and 365.7 cm^{-1} for the A and E torsional levels, respectively. The fact that the A and E values differ is probably due

TABLE III

Spectroscopic Constants of CH_3OD[a]

Constant (MHz unless noted)	A Species	E Species	Previous Value[b]
A	110249.4728(7.)	110328.7982(0.1)	110333.0912(0.4)
B	23455.27795(0.1)	23445.85972(0.4)	23448.5273(0.1)
C	21970.44521(0.1)	21978.54363(0.4)	21975.6619(0.1)
D_{ab}	-835.418176(1.)	-851.510658(0.3)	-760.36948(3.)
$F (cm^{-1}) \times 10^3$	17544.89395(10.)	17413.36728(1.)	17450.94236(1.)
ρ (unitless) $\times 10^4$	6992.079878(0.4)	6997.174975(0.003)	6997.2113l8(0.02)
$V_3 (cm^{-1})$	369.314772(0.3)	365.660135(0.05)	366.134528(0.04)
$V_6 (cm^{-1})$	0.0 (fixed)	-1.61550(0.04)	.....
F_v	-66.547191(0.01)	-66.477970(0.01)	-66.57928(0.08)
G_v	-3.151093(0.01)	-2.509178(0.001)	-2.502713(0.008)
$L_v \times 10^2$	0.0 (fixed)	-6.216723(0.6)	14.79282(3.)
$\Delta_{JK} \times 10^2$	52.066248(2.)	-8.398425(0.4)	23.25337(0.07)
$\Delta_J \times 10^3$	43.36114(0.03)	43.585217(0.07)	43.2997(0.2)
$\Delta_K \times 10^1$	-38.18882(4.0)	-1.780360(0.5)	10.4191(0.04)
k_1	-5.8836007 (fixed)	-5.8836007 (fixed)	-5.8836007(0.2)
k_2	-73.379156 (fixed)	-73.379156 (fixed)	-73.379156(0.1)
k_4	-280.797728(10.)	0.0 (fixed)	.....
$\delta_J \times 10^3$	1.380563(0.04)	3.181651(0.04)	2.93302(0.2)
$\delta_K \times 10^2$	19.65101(1.)	-38.56978(2.)	14.9013(3.)
$c_1 \times 10^2$	-78.69441(0.8)	-15.88693(3.)	-91.5654(2.)
c_2	-5.366000(0.1)	-18.020683(0.5)	.....
$H_{KJ} \times 10^3$	-32.94513(0.3)	-2.857375(0.1)	.....
$H_K \times 10^2$	0.0 (fixed)	-11.23996(0.4)	.....
$f_v \times 10^3$	1.237057(0.04)	0.0 (fixed)	.....
c_4	0.0 (fixed)	-5.7300545(0.1)	.....
d_{ab}	0.0 (fixed)	-208.366421(0.7)	-320.08603(8.)
Δ_{ab}	-15.652426(0.1)	9.1810866(0.04)	.....
δ_{ab}	4.877644(0.4)	3.768213(0.2)	.....
$g_v \times 10^4$	0.0 (fixed)	1.481252(0.07)	.....
$l_v \times 10^4$	0.0 (fixed)	2.164839(0.07)	.....
$\phi_v \times 10^1$	-24.46888(0.3)	-3.727257(0.1)	.....
$\gamma_v \times 10^2$	-26.42081(0.5)	9.368415(0.1)	.....
$\lambda_v \times 10^2$	42.944534(0.4)	0.0 (fixed)	0.511577(0.08)
$c_6 \times 10^4$	8.994204(1.)	0.0 (fixed)	.....
$c_5 \times 10^4$	1.728817(0.06)	0.0 (fixed)	.....
$c_8 \times 10^2$	-1.639704(0.2)	11.241707(0.3)	.....
$c_{10} \times 10^2$	0.0 (fixed)	-24.452619(0.3)	.....
$\delta\delta_{ab} \times 10^2$	0.0 (fixed)	-10.32806(1.)	.....
$h_{K1} \times 10^3$	0.0 (fixed)	65.89446(1.)	.....
$h_{K2} \times 10^3$	0.0 (fixed)	-6.52533(0.1)	.....
$h_{K3} \times 10^4$	0.0 (fixed)	17.16623(0.4)	.....
$d\delta_{ab} \times 10^2$	0.0 (fixed)	-48.659417(0.5)	.....
$\delta d_{ab} \times 10^2$	0.0 (fixed)	-76.554194(1.)	.....
$N_v \times 10^3$	0.0 (fixed)	-67.111949(10.)	.....
$Q_v \times 10^4$	0.0 (fixed)	-40.04805(4.)	.....
c_{11}	-6.7887569(0.2)	14.392772(0.6)	.....
$M_v \times 10^3$	41.68964(0.8)	0.0 (fixed)	.....
$\mu_v \times 10^3$	22.03966(0.2)	-2.556012(0.04)	.....
$v_v \times 10^1$	22.982768(0.4)	-3.6600609(0.05)	.....
$\theta_v \times 10^4$	-559.43285(5.)	-9.929475(0.4)	.....,

[a] Figures in parentheses represent 1σ deviations. The number of listed significant figures for each constant is necessary to reproduce calculated frequencies to 10 kHz.

[b] Reference (9).

both to the high degree of correlation among the large number of parameters needed in the separate fitting procedures and to the approximation that torsion is a one-dimensional motion (*15, 21*); there should be only one potential surface for each Born–Oppenheimer electronic state. Exceptions to the general similarity between previous and newly determined low-order constants are present. These exceptions tend to be caused by the existence of higher-order torsion–rotation interaction constants which correlate with the lower-order parameters. For example, D_{ab}, the fourth rotation constant, needed because the internal axes utilized are not the principal axes, shows different values for the A and E symmetry fits because different numbers of interaction constants from the series d_{ab}, Δ_{ab}, δ_{ab}, dd_{ab}, $\Delta\Delta_{ab}$, $\delta\delta_{ab}$, $d\delta_{ab}$, and δd_{ab}, involving the rotation operator for D_{ab} and torsional operator expressions, are used in each fit. The two newly determined D_{ab} values differ strongly from the previous values, because our previous fit contained only the one interaction constant d_{ab}. The higher-order distortion and interaction constants in our new, separate fits to the A and E data can differ radically from one another, as was the case in the revised analyses of $^{12}CH_3OH$ and $^{13}CH_3OH$.

It is interesting to compare the fit obtained here with our previous fit to microwave accuracy for the low angular momentum ($J \leqslant 8$) data of normal methanol (*2*). In general, the low-order spectroscopic constants for the A and E species tend to differ somewhat more for CH_3OD. There are two reasons for this. First, the internal a axis is at a more pronounced angle from the principal a axis in CH_3OD than it is in normal CH_3OH. The larger angle leads to a larger fourth rotation constant D_{ab}, magnifying the differences inherent in the differing interaction constant expansions. Second, although roughly the same number of spectroscopic constants are needed to fit the A species data for CH_3OD and CH_3OH, many more constants (42) are needed to fit the E species data for CH_3OD than that for CH_3OH (32). The existence of more high-order interaction constants influences the values obtained for the low-order constants.

The current extent of the fitted data for CH_3OD is still significantly smaller than that for normal methanol or its C-13 isotopomer. In the lowest torsional state, data exist only up through $J = 9$, whereas data through $J = 24$ have been measured and analyzed for the other isotopomers. In the first two excited torsional states, the only assigned data are R_a transitions ($\Delta J = 1$, $\Delta K = 0$); no transitions in which $\Delta K = \pm 1$ have been assigned. The lack of K-changing information in the excited torsional states leads to relatively large uncertainties in several of the parameters shown in Table III. More work is needed to locate the K-changing transitions, which can be strongly affected by internal rotor interactions. Experience with analyses of the other isotopomers indicates that expansion of the A and E data sets to include $\Delta K \neq 0$ transitions in the $v_t = 1, 2$ torsional states will allow determination of the lower-order torsional-rotation parameters (e.g., the Kirtman interaction constants). In turn, the number of higher-order interaction terms can then be reduced. Thus, predictions from this analysis should be viewed with caution.

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