

The Analysis of the Rotational Spectrum of Methanol to Microwave Accuracy

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A method for the analysis and characterization of a large number of rotational-torsional transition frequencies of methanol (CH_3OH) to microwave accuracy is presented. It is based on our earlier work which used a direct diagonalization of an internal axis method Hamiltonian. In the work reported here the analyses of the *A* and *E* symmetry species were separated and careful attention was paid to the selection of cross terms between rotational and torsional operators to be included in the Hamiltonian. In order to facilitate comparison, the previous data set, which contained 470 rotational transitions, was also used for this new work. In our original analysis the root-mean-square (rms) deviation was 1.2 MHz. This same data set was subsequently reanalyzed by Nakagawa, Tsunekawa, and Kojima with an effective Hamiltonian based on a Watson-like transformation with a larger number of adjustable parameters. Their approach reduced the rms deviation to ~ 0.6 MHz, but substantial model error remained. In the work reported here rms deviations of 0.065 MHz and 0.062 MHz for the *A* and *E* symmetry states, respectively, have been achieved. These deviations approximate experimental error, indicating that the model error has now been reduced from ~ 1 MHz to essentially zero. Of perhaps more importance, our new approach has significantly enhanced the predictive powers of the model and provides a means for an accurate characterization of the rotational-torsional spectrum of methanol. © 1989 Academic Press, Inc.

I. INTRODUCTION

This work was motivated by the desire to have a theoretical model for the analysis of the rotational-torsional spectra of methanol and methanol-like internal rotors, the model error of which would be small compared to the accuracy of microwave measurements (≤ 0.100 MHz) and which could be used to calculate "complete" spectral maps over a significant range of quantum states. Models for the rotational spectra of other classes of molecules, such as asymmetric rotors, which have these desirable properties have proved to be very important both for applications such as radio astronomy and atmospheric science and also as bases for fundamental considerations of their spectroscopic properties.

Experimental and theoretical work on the rotational-torsional spectrum of methanol has a rich history which has been summarized up through 1984 in our earlier paper

on methanol (1). Most notable in the early work are the pioneering theoretical studies of Dennison and co-workers (2-5) in which the internal axis method (IAM) was developed and utilized, and the millimeter-wave spectral work of Lees and Baker (6) in which large numbers of rotational-torsional transitions were analyzed. In our earlier paper, we used an extended IAM treatment based closely on the work of Lees and Baker (6) to fit 470 lines of the rotational-torsional spectrum of methanol involving the quantum numbers $J \leq 8$ and $v_t \leq 2$. All transitions in the analysis involved changes in rotational quantum numbers only. The overall root-mean-square (rms) deviation of the fit was 1.18 MHz and was obtained by varying 21 out of a total of 34 parameters. Although this fit did not achieve an rms deviation comparable to normal microwave accuracy (≤ 0.100 MHz), it was the first attempt at a global least-squares fit to a significant portion of the methanol data and provided a limited capability for predicting the frequencies of transitions not in the analysis. Our work on methanol was followed by similar studies on the isotopic variants $^{13}\text{CH}_3\text{OH}$ and CH_3OD (7-9).

Since the time of our initial work on methanol, significant new developments have been reported. In 1987, Nakagawa *et al.* (10) published a new analysis of the set of rotational-torsional transition frequencies collected by us (1). These authors used symmetry considerations and a Watson-like contact transformation to obtain a fourth-order effective Hamiltonian without indeterminate terms. In addition, they included more matrix elements off-diagonal in torsional quantum number (v_t). Their analysis of the data resulted in an improvement in the rms deviation to 0.57 MHz, still far above standard microwave accuracy. The authors were able to make an even more substantial improvement in the rms deviation to the rotational-torsional spectrum of methyl mercaptan compared with our work (11). Another important development has been the extension of the analysis of the methanol spectrum to significantly higher rotational quantum numbers. Using the same IAM approach as Herbst *et al.* (1), Sutton and Herbst (12) managed to fit 783 rotational-torsional lines out to $J = 22$ by varying 32 out of a total of 34 parameters. Their analysis required supercomputer implementation and has proved useful to astronomers interested in predictions of rotational-torsional spectral lines with large values of the rotational quantum number J . Sutton and Herbst (12) were also able to fit series of spectral lines that could not be fit in the analysis of Herbst *et al.* (1) because their larger data set allowed them to vary more parameters. Still, the rms deviation of their fit was 4.4 MHz, clearly not comparable to microwave accuracy.

The difficulties encountered in fitting the spectrum of methanol to microwave accuracy via an analysis based on a quantum mechanical Hamiltonian have given rise to an alternative procedure, first utilized by Pickett *et al.* (13). In this procedure, spectral lines are fit by suitable subtraction of empirical power series expansions for the energy levels. Pickett *et al.* (13) managed to fit 270 lines to microwave accuracy by varying 104 coefficients. More recently, Moruzzi *et al.* (14) have used the procedure to analyze a vast number of methanol lines which they measured with a high-resolution Fourier transform spectrometer in the range 8 to 100 cm^{-1} to an accuracy of $\approx 1-2$ MHz for unblended lines. These lines were analyzed along with higher resolution microwave data, primarily at lower frequencies. A glance at a small fraction of the 6725 assigned and analyzed lines in their table shows the quality of the fit to be variable but certainly not to be of microwave accuracy even for those lines measured to such accuracy. A

power series expansion has also been used to analyze the Fourier transform spectrum of methanol between 950 and 1100 cm^{-1} (15).

In this paper we present the results of a new quantum mechanical analysis of the low J ($J \leq 8$) rotational-torsional spectrum of $^{12}\text{CH}_3\text{OH}$ in its first three torsional states. Based on the significant success of Nakagawa *et al.* (10) in improving our earlier quantum mechanical analysis of the methanol spectrum, it was the goal of this work to be able to fit the data to microwave accuracy (<0.100 MHz) and to have the results of the analysis characterize the spectrum in a fashion similar to modern analyses of light asymmetric rotors. In other words, we would like to predict accurately transitions that are within the general range of the quantum numbers of the observed transitions and to be able to extrapolate with reasonable, but decreasing accuracy, as the quantum numbers of the calculated transitions move away from those of the experimental data set. These goals appear to have been met for the data set contained in Ref. (1) by use of a significantly expanded number of carefully chosen parameters and the separation, at least in our current procedure, of the previous global analysis into two distinct treatments—one for the A symmetry sublevels and one for the E symmetry sublevels. In the next section, we review briefly the IAM method used and the particular parameters added.

II. THEORY

The IAM approach used in Lees and Baker (6) and incorporated into Herbst *et al.* (1) has once again been utilized. Shown in Table I, the IAM Hamiltonian can be subdivided into rotational, torsional, and distortion terms. The rotational Hamiltonian is the standard rigid-rotor expression used for near-prolate symmetric tops (symmetry axis labeled by a) with the addition of a cross term between the angular momentum operators \mathbf{P}_a and \mathbf{P}_b , made necessary by the use of a nonprincipal axis system. It contains the four rotational constants A , B , C , and D_{ab} . The torsional Hamiltonian is the standard IAM expression in which both the torsional angular momentum \mathbf{P}_γ and \mathbf{P}_a appear because of the unusual boundary conditions chosen (16). It contains the torsional-rotational constant F and potential constants V_3 and V_6 which, when multiplied by suitable trigonometric functions, describe the height of the potential barrier to internal rotation and its angular dependence. The simplifying approximation is made that the torsional motion is one-dimensional; that is, it is described by one angle γ . An expression for the parameter ρ in the torsional Hamiltonian is given in Ref. (6). The distortion Hamiltonian, which is composed of a wide assortment of coupling terms among angular momenta and potential energy expressions, contains all of the remaining parameters. These parameters can be subdivided into groups. The "standard" distortion constants D_J , D_{JK} , D_K , δ_K , δ_J , H_J , H_{JK} , H_{KJ} , H_K , h_J , h_{JK} , h_K , L_K , L_{JK} , and P_K multiply terms in which end-over-end angular momentum operators are multiplied by one another. The three last constants multiply high powers of angular momentum operators and were not present in our previous Hamiltonian (1). In addition to the standard distortion constants, there are distortion-like expressions often referred to as "interaction" terms needed to describe the coupling between torsion and end-over-end angular momentum not reduced to zero by the transformation generating the nondistortion parts of the Hamiltonian, as shown in detail by Kirtman (17). In Table I, the great majority of these interaction terms are grouped according

TABLE I
Rotation-Torsion Hamiltonian^a

$$\begin{aligned}
 H &= H_{\text{rot}} + H_{\text{tors}} + H_{\text{dist}} \\
 H_{\text{rot}} &= 1/2 (B + C) (P_b^2 + P_c^2) + A P_a^2 + 1/2 (B - C) (P_b^2 - P_c^2) \\
 &\quad + D_{ab} \mathcal{S}(P_a P_b) \\
 H_{\text{tors}} &= E (P_\gamma + \rho P_a)^2 + 1/2 Y_3 (1 - \cos 3\gamma) + 1/2 Y_6 (1 - \cos 6\gamma) \\
 H_{\text{dist}} &= -D_J P^4 - D_{JK} P^2 P_a^2 - D_K P_a^4 - \delta_K \mathcal{S}(P_a^2 [P_b^2 - P_c^2]) - 2 \delta_J (P_b^2 - P_c^2) \\
 &\quad + H_I P^6 + H_{JK} P^4 P_a^2 + H_{KJ} P^2 P_a^4 + H_K P_a^6 + h_J P^4 (P_b^2 - P_c^2) \\
 &\quad + h_{JK} \mathcal{S}(P_a^2 [P_b^2 - P_c^2]) + h_K \mathcal{S}(P_a^4 [P_b^2 - P_c^2]) + L_K P_a^8 + L_{JK} P^4 P_a^4 + P_K P_a^{10} \\
 &\quad + (1 - \cos 3\gamma) \{ E_\nu P^2 + k_5 P_a^2 + \epsilon_2 (P_b^2 - P_c^2) + d_{ab} \mathcal{S}(P_a P_b) + f_\nu P^4 + \phi_\nu P^2 P_a^2 \\
 &\quad - 2c_6 P^2 (P_b^2 - P_c^2) - c_9 \mathcal{S}(P_a^2 [P_b^2 - P_c^2]) + h_{J1} P^4 P_a^2 + h_{K1} P^2 P_a^4 \} \\
 &\quad + \mathcal{S}(P_\gamma + \rho P_a)^2 \{ G_\nu P^2 + k_2 P_a^2 + \epsilon_J (P_b^2 - P_c^2) + \Delta_{ab} P_a P_b + g_\nu P^4 + \gamma_\nu P^2 P_a^2 \\
 &\quad - 2c_5 P^2 (P_b^2 - P_c^2) - c_8 P_a^2 (P_b^2 - P_c^2) + h_{J2} P^4 P_a^2 + h_{K2} P^2 P_a^4 \} \\
 &\quad + \mathcal{S}(P_a (P_\gamma + \rho P_a)) \{ L_\nu P^2 + k_1 P_a^2 + c_4 (P_b^2 - P_c^2) + \delta_{ab} P_a P_b + l_\nu P^4 + \lambda_\nu P^2 P_a^2 \\
 &\quad - 2c_7 P^2 (P_b^2 - P_c^2) - c_{10} P_a^2 (P_b^2 - P_c^2) + h_{J3} P^4 P_a^2 + h_{K3} P^2 P_a^4 \} \\
 &\quad + \mathcal{S}(P_\gamma + \rho P_a)^4 \{ k_4 + \epsilon_3 (P_b^2 - P_c^2) + M_\nu P^2 + (\Delta\Delta)_{ab} P_a P_b \} \\
 &\quad + k_3 P_a (P_\gamma + \rho P_a)^3 + k_6 P_a (P_\gamma + \rho P_a) (1 - \cos 3\gamma) \\
 &\quad + k_7 (P_\gamma + \rho P_a)^2 (1 - \cos 3\gamma)
 \end{aligned}$$

^a The script symbol \mathcal{S} refers to the symmetrization of operator expressions. For some factored expressions, the symbol is included before one factor and need not apply to all terms multiplying the factor.

to the torsional expression. Four different torsional expressions— $(1 - \cos 3\gamma)$, $(P_\gamma + \rho P_a)^2$, $P_a(P_\gamma + \rho P_a)$, and $(P_\gamma + \rho P_a)^4$ —are multiplied by an assortment of end-over-end angular momentum operators such as P^2 , P_a^2 , etc., each term possessing a multiplicative parameter or constant and each term properly symmetrized. Together there are now 37 different interaction terms as compared with 14 in the previous work and they contain end-over-end angular momentum operators through sixth order in the overall exponent. The current grand total of 60 available parameters is almost double the previous total of 34. However, many of these terms were not required in our final analysis and a number that were included make only small contributions. These small contributions are now observable because of the high accuracy of the fit. The letter designation of some interaction parameters is based on historical context whereas others have been newly named by us. To help keep track of what is new and what is old, we have underlined all of the parameters in Table I included in Ref. (1). Parameters in addition also *varied* in Ref. (1) are written in italics. In greatly expanding the number of available interaction terms, we have been guided by both empirical considerations (the need for specific higher order terms) and analogy with normal centrifugal distortion. We have not used a contact transformation as was done in Ref. (10) and we make no pretensions that our Hamiltonian is indeed a complete one.

As in Ref. (1), the overall Hamiltonian has been evaluated *seriatim*. First, the

torsional Hamiltonian was diagonalized using a product basis set consisting of 21 free rotor functions in the torsional degree of freedom of the type $\exp[i(3k + \sigma)\gamma]$ where $-10 \leq k \leq 10$ and $\sigma = 0$ (*A* symmetry species) or ± 1 (*E* symmetry species) multiplied by eigenfunctions $|K\rangle$ of \mathbf{P}_a . Note that since the operator \mathbf{P}_a appears in the torsional Hamiltonian, the diagonalization must be repeated for each value of K (the angular momentum along the prolate axis) desired. The resulting torsional eigenstates can be characterized by the quantum numbers $v_t = 0, 1, 2, \dots$ and K . The torsional eigenvectors were then multiplied by symmetric top basis functions to form a basis for diagonalization of the rotational and distortion–interaction parts of the Hamiltonian. The working out of individual matrix elements has been discussed by Lees and Baker (6) with ample results shown in Ref. (1) so that it need not be repeated here. Nonzero matrix elements exist that are both diagonal in the torsional quantum number v_t and connect different values of v_t . In Ref. (1), we considered matrix elements off-diagonal in v_t by ± 1 and ± 2 for those elements in which $\Delta K = \pm 1$ and ± 2 . These matrix elements are all included in the present work as well. However, the relatively small effect of the matrix elements off-diagonal in torsional quantum number v_t on our previous fit has convinced us that they are not necessary for the additional parameters contained in Table I and we have neglected them for these new parameters. The spectroscopic description of the diagonalized rotational–torsional states has been discussed in Refs. (1, 6) as have the strongly allowed transitions.

A nonlinear least-squares treatment has been utilized to fit the rotational–torsional spectral lines contained in Herbst *et al.* (1), which involve transitions with rotational

TABLE II
Transitions That Are Blends or Violate Loop Criteria

VTOR	SPECIES	J'	K'	P'	←	J''	K''	P''	FREQUENCY ^a	OBS.-CALC. ^a
1	E	1	0		←	1	1		189689.570	0.610
1	A	2	1	-	←	2	2	+	554052.056	-0.626
2	A	3	2	+	←	2	2	+	144728.700	0.343
2	A	3	2	-	←	2	2	-	144728.700	-0.375
0	E	3	-2		←	2	-2		145126.370	-0.011
0	E	3	2		←	2	2		145126.370	0.152
1	E	3	-2		←	2	-2		144728.700	-0.011
1	A	4	2	+	←	3	2	+	192963.470	-0.288
1	A	4	3	+	←	3	3	+	192963.470	0.130
1	A	4	3	-	←	3	3	-	192963.470	0.128
2	A	4	0	+	←	3	0	+	192757.650	0.096
2	E	4	-2		←	3	-2		192756.310	0.188
0	A	5	4	-	←	5	3	+	636393.568	-0.240
0	A	5	4	+	←	5	3	-	636393.568	0.274
0	A	5	3	+	←	4	3	+	241832.950	0.220
0	A	5	3	-	←	4	3	-	241832.950	-0.166
0	E	5	-2		←	4	-2		241904.119	-0.048
0	E	5	2		←	4	2		241904.407	-0.220
1	A	6	3	+	←	5	3	+	289429.750	0.446
1	A	6	3	-	←	5	3	-	282429.750	0.750
0	E	6	-2		←	5	-2		290307.563	0.243
0	E	6	2		←	5	2		290307.563	-0.183
2	E	6	0		←	5	0		289429.120	-0.579
0	A	7	1	-	←	7	1	+	23347.530	0.551
0	A	8	4	+	←	8	3	-	636304.355	1.115
0	E	8	-4		←	8	-3		524740.167	-0.314
0	E	8	-2		←	7	-1		811445.210	0.558

^a MHz

TABLE III
CH₃OH A Transitions (MHz)

VTOR	J'	K'	P'	←	J''	K''	P''	FREQUENCY	RESIDUAL
0	1	1	-	←	1	0	+	303366.890	-0.064
0	1	1	-	←	1	1	+	834.267	-0.018
0	1	0	+	←	0	0	+	48372.456	-0.014
1	1	0	+	←	0	0	+	48257.490	0.184
2	1	0	+	←	0	0	+	48192.120	0.047
0	1	1	+	←	0	0	+	350905.119	-0.020
0	2	1	-	←	2	0	+	304208.350	-0.018
0	2	1	-	←	2	1	+	2502.778	-0.005
0	2	2	-	←	2	1	+	484004.740	0.044
0	2	2	+	←	2	1	-	481504.232	0.048
1	2	1	+	←	2	2	-	553763.582	-0.067
0	2	0	+	←	1	0	+	96741.420	0.030
0	2	1	+	←	1	1	+	95914.290	-0.016
0	2	1	-	←	1	1	-	97582.830	0.026
1	2	0	+	←	1	0	+	96513.660	-0.017
1	2	1	+	←	1	1	+	96396.010	-0.048
1	2	1	-	←	1	1	-	96588.600	-0.015
2	2	0	+	←	1	0	+	96383.130	0.058
2	2	1	+	←	1	1	+	96189.670	-0.092
2	2	1	-	←	1	1	-	96553.780	0.139
0	2	1	+	←	1	0	+	398446.920	-0.055
0	2	0	+	←	1	1	+	-205791.270	0.009
0	2	2	-	←	1	1	-	579084.700	-0.018
1	2	2	+	←	1	1	+	-457367.889	-0.119
1	2	2	-	←	1	1	-	-457463.899	-0.011
0	3	1	-	←	3	0	+	305473.520	0.026
0	3	1	-	←	3	1	+	5005.321	-0.009
0	3	2	-	←	3	1	+	485263.263	0.007
0	3	2	+	←	3	1	-	480269.321	0.041
0	3	3	-	←	3	2	+	251905.812	0.078
0	3	3	+	←	3	2	-	251917.050	-0.019
1	3	1	+	←	3	2	-	553624.453	0.024
1	3	1	-	←	3	2	+	554202.988	0.065
0	3	0	+	←	2	0	+	145103.230	0.018
0	3	1	+	←	2	1	+	143865.790	-0.001
0	3	1	-	←	2	1	-	146368.300	-0.038
0	3	2	+	←	2	2	+	145133.460	0.026
0	3	2	-	←	2	2	-	145124.410	0.059
1	3	0	+	←	2	0	+	144768.200	0.022
1	3	1	+	←	2	1	+	144589.820	-0.036
1	3	1	-	←	2	1	-	144878.580	-0.017
2	3	0	+	←	2	0	+	144571.970	0.046
2	3	1	+	←	2	1	+	144281.780	-0.074
2	3	1	-	←	2	1	-	144827.610	0.006
0	3	1	+	←	2	0	+	445571.414	0.037
0	3	0	+	←	2	1	+	-156602.420	-0.047
0	3	2	+	←	2	1	+	629140.493	0.092
0	3	2	-	←	2	1	-	626626.302	0.038
0	3	1	-	←	2	2	-	-335133.513	0.062
0	3	3	+	←	2	2	+	397039.090	-0.059
0	3	3	-	←	2	2	-	397041.410	-0.029
1	3	2	+	←	2	1	+	-409035.534	-0.063
1	3	2	-	←	2	1	-	-409323.292	0.135
0	4	1	-	←	4	0	+	307165.940	0.030
0	4	1	-	←	4	1	+	8341.640	0.006
0	4	2	-	←	4	1	+	486940.837	0.012
0	4	2	+	←	4	1	-	478633.272	0.025
0	4	3	-	←	4	2	+	251866.579	0.057
0	4	3	+	←	4	2	-	251900.495	0.045
0	4	4	-	←	4	3	+	636420.231	0.138
0	4	4	+	←	4	3	-	636420.231	0.266
1	4	1	+	←	4	2	-	553437.476	0.022
1	4	1	-	←	4	2	+	554402.514	-0.041
0	4	0	+	←	3	0	+	193454.390	0.000
0	4	1	+	←	3	1	+	191810.490	-0.011
0	4	1	-	←	3	1	-	195146.760	-0.045
0	4	2	-	←	3	2	-	193488.030	-0.040
0	4	3	+	←	3	3	+	193471.520	0.070
0	4	3	-	←	3	3	-	193471.520	-0.041
1	4	0	+	←	3	0	+	193019.870	-0.005
1	4	1	+	←	3	1	+	192778.520	-0.059
1	4	1	-	←	3	1	-	193163.330	-0.060
1	4	2	-	←	3	2	-	192965.530	-0.024
2	4	1	+	←	3	1	+	192370.480	-0.119
2	4	1	-	←	3	1	-	193098.290	0.152
2	4	2	+	←	3	2	+	192613.090	0.002
2	4	2	-	←	3	2	-	192613.090	-0.012

TABLE III—Continued

VTOR	J'	K'	P'	←	J''	K''	P''	FREQUENCY	RESIDUAL
2	4	3	+	←	3	3	+	192739.440	-0.023
2	4	3	-	←	3	3	-	192739.440	-0.023
0	4	1	+	←	3	0	+	492278.713	0.047
0	4	0	+	←	3	1	+	-107013.850	-0.075
0	4	2	+	←	3	1	+	678785.455	0.073
0	4	2	-	←	3	1	-	673745.931	-0.065
0	4	1	+	←	3	2	+	-293463.990	0.119
0	4	1	-	←	3	2	-	-285111.150	-0.029
0	4	2	+	←	3	3	+	-58394.940	0.003
0	4	2	-	←	3	3	-	-58429.010	0.008
1	4	2	+	←	3	1	+	-360661.433	0.136
1	4	2	-	←	3	1	-	-361236.476	-0.006
0	5	1	-	←	5	0	+	309290.400	0.066
0	5	1	-	←	5	1	+	12511.000	-0.221
0	5	2	-	←	5	1	-	489036.955	0.045
0	5	2	+	←	5	1	+	476605.142	0.008
0	5	3	-	←	5	2	+	251811.882	-0.060
0	5	3	+	←	5	2	-	251890.901	0.028
1	5	1	+	←	5	2	-	553201.597	0.028
1	5	1	-	←	5	2	+	554651.031	0.044
0	5	0	+	←	4	0	+	241791.430	0.045
0	5	1	+	←	4	1	+	239746.250	0.029
0	5	1	-	←	4	1	-	243915.830	0.021
0	5	2	+	←	4	2	+	241887.700	0.004
0	5	2	-	←	4	2	-	241842.320	0.013
0	5	4	+	←	4	4	+	241806.510	0.065
0	5	4	-	←	4	4	-	241806.510	0.066
1	5	0	+	←	4	0	+	241267.880	0.050
1	5	1	+	←	4	1	+	240960.560	0.023
1	5	1	-	←	4	1	-	241441.240	-0.025
1	5	2	+	←	4	2	+	241192.810	-0.023
1	5	2	-	←	4	2	-	241196.350	-0.073
1	5	3	+	←	4	3	+	241198.290	0.003
1	5	3	-	←	4	3	-	241198.290	-0.003
2	5	0	+	←	4	0	+	240938.940	0.052
2	5	1	+	←	4	1	+	240454.850	-0.031
2	5	1	-	←	4	1	-	241364.120	0.021
2	5	2	+	←	4	2	+	240757.910	0.010
2	5	2	-	←	4	2	-	240757.910	-0.019
2	5	3	+	←	4	3	+	240916.160	0.012
2	5	3	-	←	4	3	-	240916.160	0.013
0	5	1	+	←	4	0	+	538570.582	0.085
0	5	0	+	←	4	1	+	-57032.920	-0.029
0	5	2	+	←	4	1	+	728862.523	-0.054
0	5	2	-	←	4	1	-	720441.236	-0.262
0	5	1	+	←	4	2	+	-247228.693	-0.034
0	5	1	-	←	4	2	-	-234683.390	-0.008
1	5	2	+	←	4	1	+	-312247.354	-0.038
1	5	2	-	←	4	1	-	-313203.428	0.010
0	6	1	-	←	6	0	+	311852.640	0.056
0	6	1	-	←	6	1	+	17513.341	-0.021
0	6	2	-	←	6	1	+	491550.827	-0.001
0	6	2	+	←	6	1	-	474196.319	0.011
0	6	3	-	←	6	2	+	251738.520	0.118
0	6	3	+	←	6	2	-	251895.728	0.030
0	6	4	+	←	6	3	-	636363.843	-0.203
1	6	1	+	←	6	2	-	552915.356	0.023
1	6	1	-	←	6	2	+	554947.481	0.001
0	6	0	+	←	5	0	+	290110.666	0.002
0	6	1	+	←	5	1	+	287670.835	0.060
0	6	1	-	←	5	1	-	292672.890	-0.025
0	6	2	+	←	5	2	+	290264.150	0.061
0	6	2	-	←	5	2	-	290184.690	-0.003
0	6	3	+	←	5	3	+	290189.510	-0.009
0	6	3	-	←	5	3	-	290190.540	-0.009
0	6	4	+	←	5	4	+	290161.140	-0.160
0	6	4	-	←	5	4	-	290161.140	-0.157
0	6	5	+	←	5	5	+	290145.090	0.017
0	6	5	-	←	5	5	-	290145.090	0.017
1	6	0	+	←	5	0	+	289511.110	0.004
1	6	1	+	←	5	1	+	289134.050	0.008
1	6	1	-	←	5	1	-	289710.460	-0.033
1	6	2	+	←	5	2	+	289414.030	0.030
1	6	2	-	←	5	2	-	289420.240	-0.030
2	6	0	+	←	5	0	+	289114.820	-0.032
2	6	1	+	←	5	1	+	288533.640	0.054
2	6	1	-	←	5	1	-	289624.280	-0.000
2	6	2	+	←	5	2	+	288897.110	0.036

TABLE III—Continued

VTOR	J'	K'	P'	←	J''	K''	P''	FREQUENCY	RESIDUAL
2	6	2	-	←	5	2	-	288897.110	-0.014
2	6	3	+	←	5	3	+	289087.370	-0.000
2	6	3	-	←	5	3	-	289087.370	-0.008
0	6	1	+	←	5	0	+	584449.713	-0.174
0	6	2	+	←	5	1	+	779380.507	0.063
0	6	2	-	←	5	1	-	766710.345	-0.037
0	6	1	+	←	5	2	+	-201445.590	-0.009
0	6	1	-	←	5	2	-	-183853.000	-0.227
0	6	2	+	←	5	3	+	38452.690	0.028
0	6	2	-	←	5	3	-	38293.500	0.194
1	6	2	+	←	5	1	+	-263793.856	-0.003
1	6	2	-	←	5	1	-	-265224.400	0.025
0	7	1	-	←	7	0	+	314859.550	0.031
0	7	2	-	←	7	1	+	494481.683	0.020
0	7	2	+	←	7	1	-	471420.477	-0.005
0	7	3	-	←	7	2	+	251641.667	-0.050
0	7	3	+	←	7	2	-	251923.631	-0.023
0	7	4	-	←	7	3	+	636337.419	0.020
0	7	4	+	←	7	3	-	636333.470	-0.085
1	7	1	-	←	7	2	+	555291.142	-0.003
0	7	0	+	←	6	0	+	338408.681	-0.031
0	7	1	+	←	6	1	+	335582.005	-0.025
0	7	1	-	←	6	1	-	341415.500	-0.147
0	7	2	+	←	6	2	+	338639.939	0.118
0	7	2	-	←	6	2	-	338512.762	-0.103
0	7	3	+	←	6	3	+	338540.795	-0.025
0	7	3	-	←	6	3	-	338543.204	0.068
0	7	4	+	←	6	4	+	338512.762	0.116
0	7	4	-	←	6	4	-	338512.762	0.129
0	7	5	+	←	6	5	+	338486.337	0.007
0	7	5	-	←	6	5	-	338486.337	0.007
0	7	1	+	←	6	0	+	629921.337	0.084
0	7	0	+	←	6	1	+	44069.490	0.001
0	7	2	+	←	6	1	+	830349.412	-0.079
0	7	1	+	←	6	2	+	-156127.700	-0.060
0	7	1	-	←	6	2	-	-132621.940	-0.120
0	7	3	+	←	6	2	+	590277.688	0.010
0	7	2	+	←	6	3	+	86903.060	0.096
0	7	2	-	←	6	3	-	86615.760	0.138
1	7	2	+	←	6	1	+	-215302.201	0.011
1	7	2	-	←	6	1	-	-217299.202	-0.002
0	8	1	-	←	8	0	+	318318.793	-0.166
0	8	2	-	←	8	1	+	497828.231	0.017
0	8	2	+	←	8	1	-	468293.771	0.016
0	8	3	-	←	8	2	+	251517.262	0.074
0	8	3	+	←	8	2	-	251984.702	-0.075
0	8	4	-	←	8	3	+	636311.690	0.012
1	8	1	-	←	8	2	+	555680.931	-0.012
0	8	0	+	←	7	0	+	386681.920	-0.110
0	8	1	+	←	7	1	+	383477.880	-0.029
0	8	1	-	←	7	1	-	390141.730	0.261
0	8	2	+	←	7	2	+	387014.800	0.058
0	8	2	-	←	7	2	-	386824.430	-0.030
0	8	3	+	←	7	3	+	386885.540	-0.043
0	8	3	-	←	7	3	-	386890.120	-0.093
0	8	4	+	←	7	4	+	386859.820	-0.077
0	8	4	-	←	7	4	-	386859.820	-0.043
0	8	5	+	←	7	5	+	386820.010	-0.073
0	8	5	-	←	7	5	-	386820.010	-0.073
0	8	1	+	←	7	0	+	674990.423	-0.027
0	8	0	+	←	7	1	+	95169.440	-0.049
0	8	1	+	←	7	2	+	-111289.620	-0.069
0	8	1	-	←	7	2	-	-80993.160	0.056
0	8	3	+	←	7	2	+	638523.486	0.046
0	8	3	-	←	7	2	-	638817.830	0.103
0	8	2	+	←	7	3	+	135376.760	-0.125
0	8	2	-	←	7	3	-	134896.960	0.014
0	8	3	+	←	7	4	+	-249451.911	-0.079
0	8	3	-	←	7	4	-	-249443.402	-0.077
1	8	2	+	←	7	1	+	-166773.278	0.038
1	8	2	-	←	7	1	-	-169427.231	-0.028

quantum number $J \leq 8$ in individual torsional states through $v_t = 2$. The data set of Herbst *et al.* (1) was chosen to facilitate comparison with earlier approaches. However, the higher accuracy of the analysis reported in this paper has allowed us to detect 27

lines that should be either removed from the analysis or given lesser weight. These are listed in Table II. All of these either do not satisfy loop conditions (6) or can clearly be identified as blends. No lines were removed solely because they did not fit. The errors associated with all of these lines are small enough that they had essentially no effect on previous analyses and could be left in this analysis with no great effect.

In previous treatments of the methanol spectrum, the spectra involving the *A* and *E* symmetry species have been included in one fit and a common set of molecular constants obtained. However, the calculation of the spectra of the *A* and *E* species involves the diagonalization of separate matrices. Because of this, it was decided to divide the analysis into two pieces at the onset. The separation allows for more rapid calculation of the spectrum of each symmetry subspecies, an important advantage in the "bootstrap" process associated with the assignment and analysis of complex spectra. Along with the additional parameters, it has allowed us to remove the model error of previous approaches. It may well be that if the torsional problem were handled in greater detail by using a more realistic potential function and incorporating other degrees of freedom, there would be less of a need for the large set of interaction parameters and the decoupling of the *A* and *E* symmetry subspecies.

III. RESULTS

Tables III and IV show the data sets for the *A* and *E* symmetry species as well as the residuals (measured – calculated frequencies) obtained from the spectral constants of Table V. In Table V, all constants fixed to zero are excluded and, for comparison, our previously determined spectral constants (*I*) are also included. Inspection of the residuals in Tables III and IV shows that the rms deviations of 0.065 and 0.062 MHz, respectively, are representative of the entire fits, and that no obvious systematic residuals, characteristic of model errors, exist. The fit to the 226 *A* symmetry species transitions required the variation of 31 out of the 60 parameters in our current model, whereas the fit to the 217 *E* symmetry species transitions required the variation of 32 parameters. There is clearly still substantial redundancy in the fits.

Comparison of the newly determined parameters with previously determined spectral constants is hazardous since the newly included interaction terms can be sufficiently important to affect the value of previous constants significantly. An extreme example of the difficulty is the case of the rotation constant D_{ab} which was determined to be -77.7 (0.5) MHz in our earlier work (*I*). In this work, the $D_{ab}\mathbf{P}_a\mathbf{P}_b$ term in the Hamiltonian has been supplemented with a variety of interaction terms (those with the constants d_{ab} , Δ_{ab} , δ_{ab} , and $(\Delta\Delta)_{ab}$) containing this angular momentum operator multiplied by different torsional expressions. One can indeed think of these interaction terms as representing the torsional dependence of the D_{ab} rotational constant. In any event, their inclusion changes the meaning and value of D_{ab} . For the *A* species, the new value of D_{ab} is $+110.99$ (2.1) MHz, while the interaction constants $\Delta_{ab} = -40.1$ (0.4) MHz and $\delta_{ab} = -16.3$ (0.4) MHz are well determined. For the *E* species, the new value of D_{ab} is -111.5 (1.7) MHz, while the interaction constants $d_{ab} = 288.4$ (2.1) MHz, $\Delta_{ab} = -20.7$ (0.6) MHz, $\delta_{ab} = -8.1$ (0.3) MHz, and $(\Delta\Delta)_{ab} = 0.51$ (5) are all well determined. The other three rotation constants (*A*, *B*, *C*), and the torsional constants (*F*, ρ , V_3) are not changed dramatically from our earlier work for either the

TABLE IV
CH₃OH *E* Transitions (MHz)

VTOR	J'	K'	←	J''	K''	FREQUENCY	RESIDUAL
0	1	0	←	1	-1	157270.700	-0.123
0	1	1	←	1	0	165050.190	-0.010
0	1	0	←	0	0	48377.090	0.196
1	1	0	←	0	0	48247.890	0.329
2	1	0	←	0	0	48178.000	-0.282
0	1	-1	←	0	0	-108893.940	-0.011
1	1	1	←	0	0	-141441.280	0.120
0	2	0	←	2	-1	157276.040	0.023
0	2	1	←	2	0	165061.140	-0.014
0	2	2	←	2	1	24934.380	0.020
0	2	-1	←	1	-1	96739.390	0.025
0	2	0	←	1	0	96744.580	0.021
0	2	1	←	1	1	96755.510	-0.003
1	2	-1	←	1	-1	96501.660	-0.073
1	2	0	←	1	0	96493.590	0.058
1	2	1	←	1	1	96492.200	0.007
2	2	-1	←	1	-1	96391.090	-0.019
2	2	0	←	1	0	96355.550	0.084
2	2	1	←	1	1	96334.990	-0.019
0	2	-2	←	1	-1	520179.066	-0.024
0	2	0	←	1	-1	254015.340	-0.042
0	2	-1	←	1	0	-60531.420	0.038
0	2	1	←	1	0	261805.710	-0.003
0	2	0	←	1	1	-68305.630	0.012
0	2	2	←	1	1	121689.850	-0.022
1	2	1	←	1	0	-93196.710	0.058
0	3	-2	←	3	-1	423468.663	0.000
0	3	0	←	3	-1	157272.470	0.127
0	3	1	←	3	0	165099.310	0.048
0	3	2	←	3	1	24928.700	0.000
0	3	3	←	3	2	530647.277	0.050
1	3	0	←	3	1	189692.150	-0.007
0	3	-1	←	2	-1	145097.470	0.024
0	3	0	←	2	0	145093.750	-0.022
0	3	1	←	2	1	145131.880	0.000
1	3	-1	←	2	-1	144750.200	-0.084
1	3	0	←	2	0	144736.300	-0.021
1	3	1	←	2	1	144734.520	0.056
1	3	2	←	2	2	144733.320	-0.114
2	3	-1	←	2	-1	144583.910	-0.062
2	3	0	←	2	0	144530.560	0.106
2	3	1	←	2	1	144499.760	0.037
2	3	2	←	2	2	144579.860	-0.079
0	3	-2	←	2	-1	568566.054	-0.055
0	3	0	←	2	-1	302369.900	0.111
0	3	-1	←	2	0	-12178.600	-0.029
0	3	1	←	2	0	310193.000	-0.035
0	3	0	←	2	1	-19967.300	0.082
0	3	2	←	2	1	170060.630	0.050
0	3	1	←	2	2	120197.520	0.000
0	3	3	←	2	2	675773.439	-0.009
1	3	1	←	2	0	-44955.810	0.026
1	3	0	←	2	1	334426.590	-0.031
0	4	-4	←	4	-3	524947.234	0.021
0	4	-2	←	4	-1	423538.258	-0.021
0	4	0	←	4	-1	157246.100	0.027
0	4	1	←	4	0	165190.530	0.032
0	4	2	←	4	1	24933.470	-0.014
0	4	3	←	4	2	530610.288	0.010
1	4	0	←	4	1	189694.390	0.041
0	4	-3	←	3	-3	193488.990	-0.007
0	4	-2	←	3	-2	193511.210	-0.021
0	4	-1	←	3	-1	193441.620	0.005
0	4	0	←	3	0	193415.370	0.025
0	4	1	←	3	1	193506.600	0.020
0	4	2	←	3	2	193511.210	-0.154
0	4	3	←	3	3	193474.330	-0.084
1	4	-3	←	3	-3	192952.700	0.015
1	4	-2	←	3	-2	192962.100	-0.010
1	4	-1	←	3	-1	192996.030	-0.027
1	4	0	←	3	0	192974.360	0.022
1	4	1	←	3	1	192972.080	-0.066
1	4	2	←	3	2	192973.650	-0.253
1	4	3	←	3	3	192957.680	-0.010
2	4	-1	←	3	-1	192773.580	-0.027
2	4	0	←	3	0	192702.240	0.094
2	4	1	←	3	1	192661.130	0.043
2	4	2	←	3	2	192768.140	-0.039

TABLE IV—Continued

VTOR	J'	K'	←	J''	K''	FREQUENCY	RESIDUAL
0	4	-1	←	3	-2	-230027.060	-0.012
0	4	-2	←	3	-1	616979.984	0.090
0	4	0	←	3	-1	350687.730	0.042
0	4	-1	←	3	0	36169.240	-0.031
0	4	1	←	3	0	358605.800	-0.043
0	4	0	←	3	1	28316.030	-0.052
0	4	2	←	3	1	218440.050	-0.014
0	4	1	←	3	2	168577.860	-0.020
0	4	3	←	3	2	724121.576	-0.065
0	4	2	←	3	3	-337135.873	-0.009
1	4	0	←	3	1	382666.474	-0.021
0	5	-4	←	5	-3	524908.133	-0.029
0	5	-2	←	5	-1	423675.155	-0.035
0	5	0	←	5	-1	157178.970	-0.031
0	5	1	←	5	0	165369.440	0.074
0	5	2	←	5	1	24959.080	-0.016
0	5	3	←	5	2	530549.271	0.051
1	5	0	←	5	1	189696.750	0.117
0	5	-4	←	4	-4	241813.257	-0.037
0	5	-3	←	4	-3	241852.352	0.007
0	5	-1	←	4	-1	241767.224	-0.031
0	5	0	←	4	0	241700.219	0.037
0	5	1	←	4	1	241879.073	0.023
0	5	3	←	4	3	241843.646	0.041
0	5	4	←	4	4	241829.646	0.037
1	5	-3	←	4	-3	241179.900	0.084
1	5	-2	←	4	-2	241187.400	0.051
1	5	-1	←	4	-1	241238.160	0.035
1	5	0	←	4	0	241205.990	-0.004
1	5	1	←	4	1	241203.690	-0.020
1	5	2	←	4	2	241210.680	-0.254
1	5	3	←	4	3	241166.530	0.000
2	5	-2	←	4	-2	240936.730	0.101
2	5	-1	←	4	-1	240958.800	-0.136
2	5	0	←	4	0	240869.490	0.045
2	5	1	←	4	1	240817.940	-0.045
2	5	2	←	4	2	240952.070	-0.003
0	5	-3	←	4	-4	-283094.900	-0.032
0	5	-1	←	4	-2	-181771.050	-0.026
0	5	-2	←	4	-1	665442.450	0.004
0	5	0	←	4	-1	398946.230	-0.026
0	5	-1	←	4	0	84521.210	0.028
0	5	1	←	4	0	407069.553	0.005
0	5	2	←	4	1	266838.130	-0.016
0	5	1	←	4	2	216945.600	0.033
0	5	3	←	4	2	772453.803	-0.080
0	5	2	←	4	3	-288705.567	0.048
1	5	1	←	4	0	51509.280	-0.081
1	5	0	←	4	1	430900.319	-0.024
0	6	-4	←	6	-3	524860.820	-0.032
0	6	-2	←	6	-1	423912.696	-0.036
0	6	0	←	6	-1	157048.620	-0.008
0	6	1	←	6	0	165678.770	0.090
0	6	2	←	6	1	25018.140	0.019
0	6	3	←	6	2	530454.695	0.033
0	6	-5	←	5	-5	290117.815	0.107
0	6	-4	←	5	-4	290162.430	-0.016
0	6	-3	←	5	-3	290209.700	-0.056
0	6	-1	←	5	-1	290069.824	0.049
0	6	0	←	5	0	289939.477	0.075
0	6	1	←	5	1	290248.762	0.045
0	6	3	←	5	3	290213.238	0.054
0	6	4	←	5	4	290183.210	-0.056
0	6	5	←	5	5	290138.890	0.014
1	6	-3	←	5	-3	289399.590	0.003
1	6	-2	←	5	-2	289402.490	0.089
1	6	-1	←	5	-1	289475.610	0.051
1	6	1	←	5	1	289427.600	-0.028
1	6	2	←	5	2	289443.930	0.266
1	6	3	←	5	3	289355.020	0.015
2	6	-2	←	5	-2	289111.350	-0.091
2	6	-1	←	5	-1	289138.820	-0.063
2	6	0	←	5	0	289031.290	0.038
2	6	1	←	5	1	288969.290	-0.010
2	6	2	←	5	2	289130.620	0.089
0	6	-3	←	5	-4	-234698.450	-0.044
0	6	-1	←	5	-2	-133605.500	-0.085
0	6	-2	←	5	-1	713982.470	-0.037

TABLE IV—Continued

VTOR	J'	K'	←	J''	K''	FREQUENCY	RESIDUAL
0	6	-1	←	5	0	132890.790	0.015
0	6	1	←	5	0	455618.116	0.033
0	6	0	←	5	1	124569.970	-0.067
0	6	2	←	5	1	315266.830	-0.007
0	6	1	←	5	2	265289.650	0.029
0	6	3	←	5	2	820762.501	0.097
0	6	2	←	5	3	-240241.502	-0.023
1	6	1	←	5	0	99730.900	-0.095
1	6	0	←	5	1	479126.480	0.147
0	7	-4	←	7	-3	524804.969	-0.071
0	7	0	←	7	-1	156828.520	0.000
0	7	1	←	7	0	166169.210	0.070
0	7	2	←	7	1	25124.880	0.060
0	7	3	←	7	2	530316.196	-0.009
0	7	-5	←	6	-5	338456.499	0.007
0	7	-4	←	6	-4	338504.099	-0.132
0	7	-3	←	6	-3	338559.928	-0.115
0	7	-2	←	6	-2	338722.940	-0.010
0	7	-1	←	6	-1	338344.628	0.001
0	7	0	←	6	0	338124.502	-0.017
0	7	1	←	6	1	338614.999	0.020
0	7	2	←	6	2	338721.630	-0.048
0	7	3	←	6	3	338583.195	-0.025
0	7	4	←	6	4	338530.249	0.018
0	7	5	←	6	5	338475.290	-0.006
0	7	-3	←	6	-4	-186300.950	-0.141
0	7	-1	←	6	-2	-85567.970	0.135
0	7	-2	←	6	-1	762635.948	0.266
0	7	-1	←	6	0	181296.030	0.031
0	7	1	←	6	0	504293.685	0.026
0	7	0	←	6	1	172445.950	0.111
0	7	2	←	6	1	363739.820	0.022
0	7	1	←	6	2	313596.840	-0.018
0	7	3	←	6	2	869037.809	-0.073
0	7	2	←	6	3	-191733.050	-0.065
1	7	1	←	6	0	147943.630	-0.038
1	7	0	←	6	1	527342.624	0.050
0	8	-2	←	8	-1	424857.263	-0.042
0	8	0	←	8	-1	156488.950	0.055
0	8	1	←	8	0	166898.650	0.024
0	8	2	←	8	1	25294.410	0.129
0	8	3	←	8	2	530123.294	-0.041
1	8	0	←	8	1	189700.490	-0.208
0	8	-5	←	7	-5	386788.660	-0.074
0	8	-4	←	7	-4	386837.700	0.279
0	8	-3	←	7	-3	386901.950	-0.067
0	8	-2	←	7	-2	387153.550	-0.026
0	8	-1	←	7	-1	386587.270	-0.056
0	8	0	←	7	0	386247.660	-0.041
0	8	1	←	7	1	386977.140	-0.048
0	8	2	←	7	2	387146.560	-0.089
0	8	3	←	7	3	386953.820	0.041
0	8	4	←	7	4	386869.410	0.023
0	8	5	←	7	5	386802.300	-0.157
0	8	-3	←	7	-4	-137903.060	-0.037
0	8	-1	←	7	-2	-37703.720	0.009
0	8	-1	←	7	0	229758.760	-0.046
0	8	1	←	7	0	553146.296	-0.031
0	8	2	←	7	3	-143169.500	0.056
1	8	1	←	7	0	196146.210	-0.007
1	8	0	←	7	1	575547.119	0.003

A or *E* symmetry species although the newly determined constants for the *E* species do differ more from our previous results, as can be seen in Table V. This pattern does not necessarily hold for the distortion and interaction constants. In order to facilitate comparisons among the fits, the values of k_1 – k_6 were fixed at the same values as in our earlier analysis.

An important measure of a spectral analysis is its ability to predict lines that are not included in the fit. As a test we have removed 20 lines from the analyses and predicted them on the basis of an analysis of the remaining lines. These lines were

chosen to include the ones that should be the hardest to predict, that is, high J , high K lines, K changing transitions, and lines in the excited torsional states. Table VI shows the results. It can be seen that the differences are comparable with expected experimental error. We conclude that it is now possible to calculate "complete" spectral maps for methanol within the range of the experimental data and that, with care, modest extrapolations should be possible.

Is it really necessary to decouple the analyses of the A and E symmetry states as we have done here? Preliminary tests with our current program have yielded an rms deviation to the global data set of Ref. (1) of ≈ 0.160 MHz with the variation of 49 parameters. This represents a reduction of almost an order of magnitude in the model error of our previous approach and a factor of 3–4 improvement on the result of Nakagawa *et al.* (10). Evidence exists that a modest expansion of our current program would also provide analyses with no evidence of model error. Although this is of significant theoretical interest, it may well be that separate A and E analyses will remain the method of choice for the analysis and characterization of methanol and methanol-like spectra.

It is interesting to consider taking this process one step farther and to perform analyses on individual torsional states. Because this requires fewer constants and at the same time is numerically stable, we have found in several preliminary studies that this is a good way to start the bootstrap procedure that is inherent in the measurement, assignment, and analysis of complex spectra.

IV. DISCUSSION

The most important result of this work is that it provides a straightforward means of analyzing the spectrum of methanol (and presumably similar species like methyl mercaptan) to microwave accuracy in a way analogous to the methods that have been developed over the years for asymmetric rotors. As a practical matter this means that complete spectral maps with statistically meaningful calculated uncertainties can be obtained from an experimental subset of the spectrum. Furthermore, theory provides a redundancy and cross check against measurement or assignment error that is unavailable in a purely experimental spectrum. In exchange for the characterization accuracy obtained for methanol two prices are paid. Although substantial redundancy is retained, the total number of constants used to characterize the A and E spectra is larger than with a global analysis. This first price is more apparent than real, because many of the additional higher order constants are a result of the added precision of the fit which allows (and requires) a more careful centrifugal distortion and interaction treatment because the small contributions of higher order parameters are now determinable. The second price is that the separation of the problem into A and E symmetry parts is an acknowledgment that the model has moved away from its geometric roots and that the parameters are becoming to a greater or lesser extent fitting parameters.

It is interesting to consider the historical context of our approach to the spectrum of a complex and floppy species. Many years ago Wilson and Howard (18) and Nielsen (19) formulated general theories of centrifugal distortion for asymmetric rotors. The theories were closely coupled to the geometry and force constants of the molecules and provided relationships among these and spectroscopic observables such as rotational constants, centrifugal distortion parameters, vibrational frequencies, and the

TABLE V
Spectral Constants of CH₃OH^a

Constant (MHz unless noted)	A Species	E Species	Previous Value ^b
A	127631.7339(242)	127631.5055(157)	127630.7538(1583)
B	24685.96292(10083)	24694.4626(5836)	24684.1785(2751)
C	23763.62765(10365)	23755.2881(5816)	23765.3680(2738)
D _{ab}	110.9888(2.0851)	-111.5105(1.7013)	-77.6655(4671)
F (cm ⁻¹)	27.633738302(8856)	27.63316276(6910)	27.63354173(3533)
ρ (unitless)	0.8097457727(316)	0.8097463650(438)	0.8097451117(1452)
V ₃ (cm ⁻¹)	373.0881039(2203)	373.0684626(26016)	373.0839507(9174)
V ₆ (cm ⁻¹)	-0.80(fixed)	-0.778560(3431)	-0.80(fixed)
F _v	-71.30036(1036)	-71.55603(441)	-71.43105(2521)
G _v	-3.562297(904)	-3.559603(1301)	-3.535184(2482)
L _v × 10 ²	16.7177(2009)	8.26671(13467)	4.01084(30762)
D _J × 10 ²	5.08701(571)	5.08124(624)	4.9768(284)
D _{JK} × 10 ¹	2.94771(2307)	2.88313(469)	2.86082(3103)
D _K	1.262907(1992)	1.146639(3601)	1.058349(23160)
k ₁	-3.8(fixed)	-3.8(fixed)	-3.8(fixed)
k ₂	-80.0(fixed)	-80.0(fixed)	-80.0(fixed)
k ₃	-132.0(fixed)	-132.0(fixed)	-132.0(fixed)
k ₄	-249.0(fixed)	-249.0(fixed)	-249.0(fixed)
k ₅	161.0(fixed)	161.0(fixed)	161.0(fixed)
k ₆	884.0(fixed)	884.0(fixed)	884.0(fixed)
δ _J × 10 ⁴	11.2904(3031)	20.2564(1.7393)	0.0(fixed)
δ _K × 10 ¹	-8.31145(1.04956)	1.94605(30363)	-7.5071(1.1932)
c ₁	-1.209498(26794)	-1.745366(45686)	-1.22722(9944)
c ₂	0.89245(13976)	-2.003480(362507)	1.1392(2378)
H _{JK} × 10 ⁴	0.0(fixed)	0.0(fixed)	-2.8164(4998)
H _{KJ} × 10 ⁴	-18.8750(2.3321)	-1.96915(28994)	9.42500(1.66993)
H _K × 10 ²	0.0(fixed)	-0.682732(18592)	-1.071236(92898)
h _K × 10 ²	-2.52008(44548)	0.0(fixed)	-5.92119(87581)
f _v × 10 ⁴	8.433(813)	0.0(fixed)	0.0(fixed)
c ₃ × 10 ²	0.0(fixed)	-4.25410(75599)	-1.4695(6582)
c ₄	-0.928105(116277)	-1.91685(23437)	

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

^b Reference (1).

TABLE V—Continued

Constant (MHz unless noted)	A Species	E Species	Previous Value ^b
d_{ab}	0.0(fixed)	288.3602(2.0663)	
Δ_{ab}	-40.11431(40862)	-20.68134(64366)	
δ_{ab}	-16.3033(4038)	-8.1222(2928)	
$g_v \times 10^4$	0.0(fixed)	0.4343(1039)	
$l_v \times 10^4$	0.0(fixed)	0.5552(2172)	
$\phi_v \times 10^2$	1.6819(4369)	0.0(fixed)	
$\gamma_v \times 10^3$	0.0(fixed)	2.1418(1500)	
$\lambda_v \times 10^3$	-8.52825(17441)	0.0(fixed)	
$c_5 \times 10^4$	1.0681(551)	0.0(fixed)	
$c_8 \times 10^1$	1.14309(13366)	0.0(fixed)	
$c_9 \times 10^1$	-0.92510(69967)	0.0(fixed)	
$h_{K1} \times 10^3$	2.86563(34948)	0.0(fixed)	
$h_{K2} \times 10^4$	6.85703(31220)	0.8424(1589)	
$h_{K3} \times 10^4$	0.0(fixed)	0.6530(1075)	
$L_{JK} \times 10^6$	-4.7835(9214)	0.0(fixed)	
$M_v \times 10^4$	0.0(fixed)	21.2925(5228)	
$(\Delta\Delta)_{ab}$	0.0(fixed)	0.508546(50791)	

like. Indeed, much of the thrust of molecular spectroscopy has been devoted toward the inversion of spectroscopic parameters to obtain molecular properties. However, modern spectroscopic techniques produce bodies of data with an accuracy that far exceeds that of the theory (except perhaps for simple molecules like diatomics) which binds the fundamental properties of a molecule to its spectroscopic features. Spectroscopists must then utilize analysis techniques that are not so tightly coupled to basic molecular properties. For example, current practice in asymmetric rotors is to fit the rotational spectrum of each vibrational state to its own set of rotational and distortion constants. In this case, for the lowest order constants, relations to the geometric basis exist (but not uniquely), but the operators that are the coefficients of the higher order constants were obtained by logical extension of the lower order terms in the power series (20). An alternative procedure would be to build into the Hamiltonian a suitable dependence on vibrational state so that effectively the rotational and distortion constants change with vibrational state. This second procedure is what is accomplished in our extended IAM Hamiltonian. The interaction terms contain the torsional dependence of the more "fundamental" rotational and distortion terms. Although they can be justified and given explicitly by basic theory (17), they are used here to reduce data sets of high accuracy so that additional spectral lines can be calculated accurately.

It is unclear at the present time how and if the number of interaction terms needed

TABLE VI
Observed Transitions Predicted by Fit

VTOR	SPECIES	J'	K'	P'	←	J''	K''	P''	FREQUENCY ^a	OBS.-CALC. ^a
0	A	4	2	-	←	3	1	-	673745.931	-0.073
1	E	5	3	-	←	4	3	-	241166.530	-0.013
1	A	6	1	-	←	5	1	-	289710.460	-0.035
1	A	6	2	+	←	5	2	+	289414.030	0.028
2	A	6	3	+	←	5	3	+	289087.370	-0.043
2	A	6	3	-	←	5	3	-	289087.370	-0.042
0	E	6	5	-	←	5	5	-	290138.890	0.017
1	E	6	3	-	←	5	3	-	289335.020	-0.030
0	E	7	-3	-	←	6	-3	-	338559.928	-0.119
0	E	7	-4	-	←	7	-3	-	524804.969	-0.104
0	A	8	5	+	←	7	5	+	386820.010	-0.197
0	A	8	5	-	←	7	5	-	386820.010	-0.197
0	E	8	4	-	←	7	4	-	386869.410	0.029
0	A	8	3	-	←	7	2	-	638817.830	0.104
0	A	8	3	-	←	7	4	-	-249443.402	-0.096
0	A	8	2	-	←	7	1	-	-169427.231	-0.054
0	E	8	-3	-	←	7	-4	-	-137903.060	-0.009
1	E	8	0	-	←	7	1	-	575547.119	-0.042
0	A	8	3	+	←	8	2	-	251984.702	-0.081
0	E	8	3	-	←	8	2	-	530123.294	-0.091

^a MHz

in our current treatment can be significantly reduced. Perhaps a careful treatment of higher order terms in the Hamiltonian akin to the complete fourth-order Hamiltonian previously derived (10) can achieve such a reduction. The inclusion of more off-diagonal terms in v_t , the torsional quantum number, might be useful. Another possibility previously alluded to is a more accurate treatment of the torsional problem. Careful ab initio treatments of the internal rotor HSSH (21, 22) show that at least one other geometrical parameter (the SSH bond angle) changes substantially as the internal rotor undergoes torsional motion. It is probable that similar effects occur in other internal rotors, in which case the torsional Hamiltonian should include them. An inaccurate torsional Hamiltonian clearly affects the final rotational-torsional eigenstates obtained.

Convergence in any spectroscopic model is always an important issue. We see no evidence at this time that our approach cannot be extended to transitions of higher J and K , subject to limitations similar to those on other species with similar rotational constants. It will be interesting to see how rapidly higher order centrifugal distortion and interaction parameters will need to be added to the analysis with increasing J and K in the data set. In any event, the spectrum of methanol is so rich that substantial redundancy in the fit should not be a problem even if the high order centrifugal distortion parameters that are now common in the analysis of light asymmetric rotors are required. In addition to extending the model to include transitions of higher J and K , it is of interest to determine whether or not a global model of the methanol spectrum that achieves microwave accuracy can be obtained. As mentioned above, currently we have not yet succeeded in obtaining such a model although there is every indication that with a reexamination of the interaction parameters included in the Hamiltonian we will be able to achieve this goal.

In summary, a means of characterizing the spectrum of methanol to microwave

accuracy has been presented. This method should prove to be especially valuable for applications, such as radio astronomy, where it is important to have complete spectral maps of assigned lines. In addition, our analysis, by accurately characterizing a large body of data with substantial redundancy, should provide useful information for attempts at reconciling all methanol data in terms of a single global theoretical model.

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