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A New Analysis and Additional Measurements of the Millimeter and Submillimeter Spectrum of Methanol

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Over 100 new spectral lines of gas-phase methanol in the millimeter and submillimeter region (viz. 150–1000 GHz) corresponding to rotational transitions in the two lowest torsional states have been measured and assigned. Some of these lines have been combined with spectral lines measured by previous investigators below 1000 GHz into a global data set consisting of 470 lines involving transitions with $J \leqslant 8$ and v_t (torsional quantum number) $\leqslant 2$, and then analyzed via a nonlinear least-squares procedure. The analysis involves supplementing the standard IAM Hamiltonian with a number of new distortion and "interaction" constants. Direct diagonalization has been employed in preference to an earlier perturbation scheme. The quality of the least-squares fit compares favorably with the previous quantum mechanical approach. © 1984 Academic Press, Inc.

I. INTRODUCTION

The rotational–torsional spectrum of methanol, one of the simplest asymmetric rotors with internal rotation, has been studied by a large number of investigators in both the microwave and infrared regions of the spectrum. Among the early microwave studies are those of Hughes *et al.* (*1*), Venkataswarlu *et al.* (*2*), Dreizler and Rudolph (*3*), and Rudolph *et al.* (*4*). In 1968, Lees and Baker (*5*) measured an extensive number of both *a*-type and *b*-type spectral lines at frequencies up to 200 GHz. During the 1970's, some high-resolution (*6, 7*) and interstellar studies (*8*) of methanol spectra in the microwave were undertaken, while Johnston and Srivastawa (*9*) and Johnston *et al.* (*10*) reported laser Stark measurements in the 800-GHz region. More recently, methanol spectra involving torsionally excited states have been reported in the Orion interstellar source (*11, 12*), and dipole moment mesurements along both *a* and *b* axes were accurately measured in the laboratory via microwave Stark spectroscopy (13) and ir-microwave double resonance (*14*). In 1981, Pickett *et al.* (*15*) published 126 new spectral lines of methanol in the region 200–850 GHz involving transitions in the ground torsional state. Finally, Sastry *et al.* (*16*) have measured and assigned many transitions at frequencies up to 400 GHz involving the first three torsional states of methanol. Most of their measurements were accomplished in our laboratory.

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In addition to these experimental studies, advances have been made in the theoretical understanding of the rotational–torsional spectrum of methanol. Early work by Dennison and co-workers (*17–19*) led to an understanding of the general features of the spectrum. The detailed features of the spectrum were treated by Kivelson (*20, 21*), Nishikawa (*22*), Hecht and Dennison (*23*), and Swan and Strandberg (*24*). Refinements to the detailed theory were made by Kirtman (*25*), and were utilized in spectral analysis by Kwan and Dennison (*26*) and Lees and Baker (*5*). These latter authors applied the detailed theory in a systematic manner to their millimeter data. They fit *a*-type and *b*-type spectra separately, and treated asymmetry and torsional effects via perturbation theory. In order to fit the *b*-type spectra, Lees and Baker (*5*) included infrared data in their analysis. The accuracy of their approach (*5, 16, 27*) is often sufficient to assign spectral lines, but does not approach the quality of least-squares fits to normal, semirigid asymmetric top data, where agreement between observed and calculated frequencies is customarily ≤ 100 kHz.

The purpose of this paper is twofold. First, a number of new millimeter and submillimeter lines of methanol involving the two lowest torsional states are reported. The measured lines were selected for study based on Fortrat diagrams that showed which were the most salient transitions not yet studied in this frequency region with angular momentum $J \leq 15$. Second, these lines and those of previous investigators have been combined into a global data set which includes 470 transitions involving $J \leq 8$ and $v_t \leq 2$. The data set has been analyzed via an essentially nonperturbative diagonalization procedure involving an extended IAM ("internal axis method") Hamiltonian. Our least-squares fit to this data set has a root-mean-square deviation of 1.2 MHz and, although better than the earlier perturbative approach, is still not comparable in quality with customary analyses of semirigid molecules.

II. EXPERIMENTAL DETAILS

The measurements of methanol spectral lines have been accomplished with our standard millimeter and submillimeter techniques, described elsewhere in the literature (*28, 29*). All measurements were made with phase-locked klystrons and lock-in detection techniques. The data were collected, processed, and measured via a computer.

III. THEORY

The internal axis method (IAM) has been employed with identical phase conventions to those of Lees and Baker (*5*). The Hamiltonian used by these authors has been supplemented with a variety of new distortion and "interaction" constants. Contained in Table I, this Hamiltonian can be divided into rotation ($\hat{H}_{\rm rot}$), torsion ($\hat{H}_{\rm tors}$), and distortion and "interaction" terms ($\hat{H}_{\rm dist}$). The torsional Hamiltonian is not completely independent of the rotational Hamiltonian, but rather contains a dependence on $\hat{P}_{\rm a}$, the angular momentum along the inertial a (figure) axis. Other parameters in the Hamiltonian expression listed in Table I are the effective rotation constants A, B, C, D_{ab}, and F; the angular momentum operators $\hat{P}^2$, $\hat{P}_b^2$, and $\hat{P}_c^2$;

TABLE I

Rotation–Torsion Hamiltonian[a]

$$
\begin{aligned}
\hat{H} &= \hat{H}_{\mathrm{rot}} + \hat{H}_{\mathrm{tors}} + \hat{H}_{\mathrm{dist}} \\
\hat{H}_{\mathrm{rot}} &= \tfrac{1}{2}(B+C)(\hat{P}_b^{\,2}+\hat{P}_c^{\,2}) + A\hat{P}_a^{\,2} + \tfrac{1}{2}(B-C)(\hat{P}_b^{\,2}-\hat{P}_c^{\,2}) \\
&\qquad + D_{ab}(\hat{P}_a\hat{P}_b + \hat{P}_b\hat{P}_a) \\
\hat{H}_{\mathrm{tors}} &= F(\hat{P}_\gamma + \rho\hat{P}_a)^2 + \tfrac{1}{2}V_3(1-\cos 3\gamma) + \tfrac{1}{2}V_6(1-\cos 6\gamma) \\
\hat{H}_{\mathrm{dist}} &= \hat{P}^2\Big\{\Big[F_v + f_v\hat{P}^2\Big](1-\cos 3\gamma) + G_v(\hat{P}_\gamma + \rho\hat{P}_a)^2 + L_v\hat{P}_a(\hat{P}_\gamma + \rho\hat{P}_a) \\
&\quad - D_J\hat{P}^2 - D_{JK}\hat{P}_a^{\,2}\Big\} + k_1\hat{P}_a^{\,3}(\hat{P}_\gamma + \rho\hat{P}_a) + k_2\hat{P}_a^{\,2}(\hat{P}_\gamma + \rho\hat{P}_a)^2 \\
&\quad + k_3\hat{P}_a(\hat{P}_\gamma + \rho\hat{P}_a)^3 + k_4(\hat{P}_\gamma + \rho\hat{P}_a)^4 + k_5\hat{P}_a^{\,2}(1-\cos 3\gamma) \\
&\quad + k_6\hat{P}_a(\hat{P}_\gamma + \rho\hat{P}_a) \times (1-\cos 3\gamma) + k_7(\hat{P}_\gamma + \rho\hat{P}_a)^2(1-\cos 3\gamma) \\
&\quad - D_K\hat{P}_a^{\,4} - 2\delta_J\,\hat{P}^2(\hat{P}_b^{\,2}-\hat{P}_c^{\,2}) - \delta_K(\hat{P}_a^{\,2}\Big[\hat{P}_b^{\,2}-\hat{P}_c^{\,2}\Big] + \Big[\hat{P}_b^{\,2}-\hat{P}_c^{\,2}\Big]\hat{P}_a^{\,2}) \\
&\quad + c_1\Big[(\hat{P}_b^{\,2}-\hat{P}_c^{\,2})(\hat{P}_\gamma + \rho\hat{P}_a)^2 + (\hat{P}_\gamma + \rho\hat{P}_a)^2(\hat{P}_b^{\,2}-\hat{P}_c^{\,2})\Big] \\
&\quad + c_2\Big[(\hat{P}_b^{\,2}-\hat{P}_c^{\,2})(1-\cos 3\gamma)\Big] + H_J\hat{P}^6 + H_{JK}\hat{P}^4\hat{P}_a^{\,2} + H_{KJ}\hat{P}^2\hat{P}_a^{\,4} \\
&\quad + H_K\hat{P}_a^{\,6} + 2h_J\hat{P}^4(\hat{P}_b^{\,2}-\hat{P}_c^{\,2}) + h_{JK}\Big[\hat{P}^2\hat{P}_a^{\,2}(\hat{P}_b^{\,2}-\hat{P}_c^{\,2}) \\
&\quad + \hat{P}^2(\hat{P}_b^{\,2}-\hat{P}_c^{\,2})\hat{P}_a^{\,2}\Big] + h_K\Big[\hat{P}_a^{\,4}(\hat{P}_b^{\,2}-\hat{P}_c^{\,2}) + (\hat{P}_b^{\,2}-\hat{P}_c^{\,2})\hat{P}_a^{\,4}\Big] \\
&\quad + c_3\Big[(\hat{P}_b^{\,2}-\hat{P}_c^{\,2})(\hat{P}_\gamma + \rho\hat{P}_a)^4 + (\hat{P}_\gamma + \rho\hat{P}_a)^4(\hat{P}_b^{\,2}-\hat{P}_c^{\,2})\Big]
\end{aligned}
$$

[a] notation follows reference 5 except that their $\hat{P}_\gamma$ has been replaced by $\hat{P}_\gamma + \rho\hat{P}_a$. The difference is due to a difference in basis set.

the torsional angular momentum operator $\hat{P}_\gamma$, where γ is the torsional angle; the torsional potential constants V_3 and V_6 which describe the height of the cos 3γ and cos 6γ contributions to the torsional potential; the centrifugal distortion constants D_J, D_{JK}, D_K, δ_J, δ_K, H_J, H_{JK}, H_{KJ}, H_K, h_J, h_{JK}, and h_K; the "interaction" constants F_v, f_v, G_v, L_v, k_1, k_2, k_3, k_4, k_5, k_6, k_7, c_1, c_2, and c_3, which describe the strength of various interactions between the rigid body angular momenta, the torsional angular momentum, and the torsional potential energy; and the unitless parameter ρ which is a function of several moments of inertia (5). The "interaction" constants c_1, c_2, c_3, and a variety of centrifugal distortion constants are used here for the first time. The new "interaction" constants describe interactions between the torsional quantities P_γ^2 and cos 3γ and the operator expression $\hat{P}_b^2 - \hat{P}_c^2$, which is related to the rigid body asymmetry.

The essence of the IAM approach is the removal of the strong coupling between the angular momentum for rigid body rotation and that associated with internal (torsional) rotation (*30*). This is a big advantage and, as shall be seen below, leads to relatively unimportant matrix elements off-diagonal in torsional state. This advantage is achieved at the expense of a slight complication in the torsional problem—instead of a simple kinetic energy term involving torsional angular momentum $\hat{P}_\gamma$ in $\hat{H}_{\text{tor}}$, the term contains the mixed angular momentum expression $\hat{P}_\gamma + \rho\hat{P}_a$, which leads to the complication that the torsional Hamiltonian must be reevaluated for different values of K, the eigenvalue of $\hat{P}_a$. It is to be noted that the Hamiltonian in Table I appears to be somewhat different from that of Lees and Baker (*5*) in terms containing $\hat{P}_\gamma$. These authors utilized a Hamiltonian that has $\hat{P}_\gamma$ in expressions where our Hamiltonian has $\hat{P}_\gamma + \rho\hat{P}_a$. Most terms with $\hat{P}_\gamma + \rho\hat{P}_a$ can be reduced to ones with $\hat{P}_\gamma$ only by suitable manipulation of the basis set used for solving the problem. This manipulation, involving a definition of single-valuedness, has been done by Lees and Baker (*5*) whereas we, as Amano (*14*), have preferred to keep the more complicated expressions to indicate more overtly the residual coupling between $\hat{H}_{\text{tor}}$ and the rigid body rotation.

The overall Hamiltonian is best evaluated in stages. First, $\hat{H}_{\text{tor}}$ is evaluated in a product basis set comprised of free rotor torsional eigenfunctions of $\hat{P}_\gamma = -i\partial/\partial\gamma$ and eigenfunctions $|K\rangle$ of $\hat{P}_a$:

$$|Kk\sigma\rangle = \frac{1}{\sqrt{2\pi}}|K\rangle \exp(i[3k + \sigma]\gamma), \tag{1}$$

where $\sigma = 1, 0, -1$ and k is any integer. The eigenvalues of $\hat{P}_\gamma$ are simply $3k + \sigma$. Because of the threefold symmetry of the torsional problem, basis functions of different σ do not mix. In addition, because

$$[\hat{H}_{\text{tors}}, \hat{P}_a] = 0, \tag{2}$$

basis functions of different K do not mix either. The resulting Hamiltonian matrix for each value of σ and K contains diagonal terms, and terms off-diagonal in k by ±1 and ±2 units. The matrix is formally infinite in size, but it was found that diagonalization of a 21×21 matrix $(-10 \leqslant k \leqslant 10)$ is sufficient to ensure the needed accuracy in the energies of the lowest torsional states. The resulting torsional eigenfunctions can be written as

$$|Kv_t\sigma\rangle = \frac{1}{\sqrt{2\pi}}|K\rangle \sum_{k=-10}^{10} A^{Kv_t}_{3k+\sigma} \exp(i[3k + \sigma]\gamma), \tag{3}$$

where $v_t = 0, 1, 2, 3, \cdots$ is the torsional vibrational quantum number and the $A^{Kv_t}_{3k+\sigma}$ are the expansion coefficients or eigenvector elements. The notation for these coefficients is that of Lin and Swalen (*30*). States with $\sigma = 0$ are labeled A whereas states with $\sigma = +1$ and -1 are labeled E_1 and E_2, respectively. For A torsional states, there is a degeneracy between $\pm K$ levels while for E states there is a degeneracy between E_1, K and E_2, $-K$ levels. We can thus refer to E_1 and E_2 levels as E levels where the sign of K is that appropriate for E_1.

The rotational and distortion Hamiltonian $(\hat{H}_{\text{rot}} + \hat{H}_{\text{dist}})$ is then evaluated in the basis set

$$|JKv_t\sigma\rangle = |JK\rangle|Kv_t\sigma\rangle, \tag{4}$$

where $|JK\rangle$ is the remaining factor of the symmetric top eigenfunction with total angular momentum J. The total matrix elements (including the diagonal torsional energy contribution) obtained in this representation are shown in Table II. Note that matrix elements off-diagonal in v_t occur for those elements with $\Delta K = \pm 1$, and ± 2. Matrix elements off-diagonal in v_t also occur for selected $\Delta K = 0$ terms of

TABLE II

Matrix Elements of Rotation–Torsion Hamiltonian

Basis Set: $|JKv_t\sigma\rangle = |JK\rangle|Kv_t\sigma\rangle$

$$|Kv_t\sigma\rangle = \frac{1}{\sqrt{2\pi}}|K\rangle \sum_{k=-10}^{10} A^{K,v_t}_{3k+\sigma} \exp(i[3k+\sigma]\gamma);\ \sigma = 1,0,-1$$

$$\langle JKv_t\sigma|\hat{H}|JKv_t\sigma\rangle = E^{\mathrm{TORS}}_{Kv_t\sigma} + \frac{1}{2}(B+C)\left[J(J+1)-K^2\right] + AK^2 + J(J+1)\left\{\left[F_v + f_v\ J(J+1)\right]\right.$$

$$\times\left(1-\sum_k A^{K,v_t}_{3(k+1)+\sigma} A^{K,v_t}_{3k+\sigma}\right) + G_v \sum_k \left(A^{K,v_t}_{3k+\sigma}\right)^2 (3k+\sigma+\rho K)^2 + L_v K \sum_k \left(A^{K,v_t}_{3k+\sigma}\right)^2 (3k+\sigma+\rho K)$$

$$\left. - D_{JK}K^2 - D_J J(J+1)\right\} + k_1 K^3 \sum_k \left(A^{K,v_t}_{3k+\sigma}\right)^2 (3k+\sigma+\rho K) + k_2 K^2 \sum_k \left(A^{K,v_t}_{3k+\sigma}\right)^2 (3k+\sigma+\rho K)^2$$

$$+ k_3 K \sum_k \left(A^{K,v_t}_{3k+\sigma}\right)^2 (3k+\sigma+\rho K)^3 + k_4 \sum_k \left(A^{K,v_t}_{3k+\sigma}\right)^2 (3k+\sigma+\rho K)^4$$

$$+ k_5 K^2\left(1-\sum_k A^{K,v_t}_{3(k+1)+\sigma} A^{K,v_t}_{3k+\sigma}\right) + k_6 K \sum_k \left(A^{K,v_t}_{3k+\sigma}\right)^2 (3k+\sigma+\rho K)$$

$$+ k_7 \left\{\sum_k \left(A^{K,v_t}_{3k+\sigma}\right)^2 (3k+\sigma+\rho K)^2 - \tfrac{1}{2} \sum_k A^{K,v_t}_{3k+\sigma} A^{K,v_t}_{3(k+1)+\sigma} \left([3k+\sigma+\rho K]^2\right.\right.$$

$$\left.\left. + [3(k+1)+\sigma+\rho K]^2\right)\right\} - D_K K^4 + H_J [J(J+1)]^3 + H_{JK}\ J^2(J+1)^2 K^2 + H_{KJ}\ J(J+1)K^4$$

$$+ H_K K^6$$

$$\langle JKv_t\sigma|\hat{H}|JK\pm 1\ v_t'\sigma\rangle = D_{ab}\sqrt{J(J+1) - K(K\pm 1)}\ (K\pm\tfrac{1}{2}) \times \sum_k A^{K,v_t}_{3k+\sigma} A^{K\pm 1,v_t'}_{3k+\sigma}$$

$$\langle JKv_t\sigma|\hat{H}|JK\pm 2\ v_t'\sigma\rangle = \left[\left\{\frac{B-C}{4} - \delta_J\ J(J+1) - \frac{\delta_K}{2}\left[K^2+(K\pm 2)^2\right]\right.\right.$$

$$+ h_J\ J^2(J+1)^2 + \frac{h_{JK}}{2} J(J+1)\left[K^2+(K\pm 2)^2\right]$$

$$\left. + \frac{h_K}{2}\left[K^4+(K\pm 2)^4\right]\right\} \sum_k A^{K,v_t}_{3k+\sigma} A^{K\pm 2,v_t'}_{3k+\sigma} + \frac{c_1}{2}\sum_k A^{K,v_t}_{3k+\sigma} A^{K\pm 2,v_t'}_{3k+\sigma} \left[(3k+\sigma+\rho K)^2\right.$$

$$\left. + (3k+\sigma+\rho(K\pm 2))^2\right] + \frac{c_2}{2}\left\{\sum_k A^{K,v_t}_{3k+\sigma} A^{K\pm 2,v_t'}_{3k+\sigma} - \tfrac{1}{2}\sum_k \left(A^{K,v_t}_{3(k+1)+\sigma} A^{K\pm 2,v_t'}_{3k+\sigma}\right.\right.$$

$$\left.\left. + A^{K,v_t}_{3k+\sigma} A^{K\pm 2,v_t'}_{3(k+1)+\sigma}\right)\right\} + \frac{c_3}{2}\sum_k A^{K,v_t}_{3k+\sigma} A^{K\pm 2,v_t'}_{3k+\sigma} \times \left[(3k+\sigma+\rho K)^4\right.$$

$$\left.\left. + (3k+\sigma+\rho(K\pm 2))^4\right]\right] \sqrt{[J(J+1) - K(K\pm 1)][J(J+1) - (K\pm 1)(K\pm 2)]}$$

$\hat{H}_{\text{dist}}$. These have not been included in the present treatment for reasons discussed below. In effect therefore, these terms of $\hat{H}_{\text{dist}}$ are treated by first-order perturbation theory. The included elements off-diagonal in v_t can be divided into two classes: those that are nonzero because of nonzero torsional overlaps of the type $\sum_{k=-10}^{10} A_{3k+\sigma}^{K,v_t} A_{3k+\sigma}^{K',v_t'}$ and those that are nonzero because of nonzero terms that involve the expansion coefficients $A_{3k+\sigma}^{K,v}$ in more complex expressions. The latter terms stem from the Hamiltonian "interaction" constants c_1, c_2, and c_3 (Table I). Details of matrix element evaluation can be found in Lees and Baker (*5*) and Lin and Swalen (*30*).

A direct diagonalization procedure has been utilized to determine the rotational–torsional eigenvalues and eigenfunctions. Matrix elements connecting $\Delta v_t = 0, \pm 1$, and ± 2 were included. Because data for $v_t = 0, 1, 2$ were used in the analysis, matrices containing $v_t = 0, 1, 2, 3$, and 4 were required for each value of J considered. The dimension of the rotational–torsional matrix for a given value of J is then $[(2J + 1) \times 5] \times [(2J + 1) \times 5]$.

The diagonalized rotational–torsional A states ($\sigma = 0$) can be classified as "+" or "−" (*5, 19*), where the designations "±" refer respectively to the $|JKv_t0\rangle \pm |J, -K, v_t0\rangle$ and $|JKv_t0\rangle \mp |J, -K, v_t0\rangle$ linear combinations of basis set functions for K even and K odd. These descriptions do not refer to the *overall* parities of the levels which are $\pm(-1)^{J+v_t}$. Strongly allowed transitions for methanol in the absence of torsional (v_t) changes are

$$\begin{array}{llll} A\text{ levels:} & \pm \leftrightarrow \mp & \Delta J = 0 & |\Delta K| = 0, 1 \\ (K \geq 0) & \pm \leftrightarrow \pm & |\Delta J| = 1 & |\Delta K| = 0, 1 \\ E\text{ levels:} & & \Delta J = 0 & |\Delta K| = 1 \\ & & |\Delta J| = 1 & |\Delta K| = 0, 1, \end{array} \tag{5}$$

where the K quantum number is, of course, an exact one only in the absence of asymmetry.

A nonlinear least-squares treatment has been utilized in an attempt to fit a large number of rotational–torsional transitions of methanol in the microwave, millimeter, and submillimeter regions of the spectrum. All transitions utilized do not involve changes in v_t. The number of observed spectral lines of methanol with $\Delta v_t = 0$ below 1 THz in frequency that have been measured to high accuracy (<1 MHz) and assigned is near 700. These lines can be divided into three major distinct classes: *a*-type *R*-branch transitions ($\Delta K = 0$, $\Delta J = 1$); *b*-type *Q*-branch transitions ($\Delta K = \pm 1$, $\Delta J = 0$); and *b*-type *R*- and *P*-branch transitions ($\Delta K = 1$, $\Delta J = \pm 1$). In addition, there are some *K*-doubling ($\Delta K = \Delta J = 0 + \leftrightarrow -$) transitions at low frequencies and one reported $\Delta K = -3$ *Q*-branch series (16). The *Q*-branch transitions, most of which involve $v_t = 0$ only, are grouped into closely spaced series of lines. Some *Q*-branch series have been studied up to $J = 25$–30 whereas *a*-type transitions have been measured up to $J = 8$ only. In deciding what transitions to include in our analysis, we were motivated by several factors. These included the desirability of checking certain ambiguous assignments by loop methods if possible (*5*) or by error curve analyses, the need to exclude certain lines which previous theoretical treatments and ours could not reproduce to within 5 GHz, and cost. Eventually, it was decided to include 470 lines with $J \leq 8$ subject to the above criteria. These 470 lines, consisting of 241 A transitions and 229 E transitions, involve the lowest three torsional levels ($v_t = 0, 1, 2$). All lines measured in this laboratory with $J \leqslant 8$ have been included in the data set.

IV. RESULTS AND DISCUSSION

The experimental lines fit by our analysis are listed in Tables III and IV, along with residuals and references to the original investigators. Uncertainties in the frequencies measured in this work are ±50 kHz. Other uncertainties are as noted by past investigators, except that all uncertainties less than ±50 kHz are set at this value. The overall root-mean-square deviation of the fit, 1.18 MHz, was obtained by varying 21 out of 34 constants in the analysis and fixing the others either at zero or at values obtained by Lees and co-workers (*5, 27*). Parameters determined by this procedure are listed in Table V. Agreement with previous determinations (*2, 5, 27*) is quite good, with our standard deviations being somewhat smaller. Lees and co-workers (*5, 27*) obtained the "Kirtman interaction" constants k_1–k_7 and the potential energy parameter V_6 by including infrared data in their fit. (See also Kwan and Dennison (*26*).) In our fit, we were able to vary k_1, k_3, k_4, k_6, and V_6 independently, but obtained large uncertainties in these parameters and did not improve the quality of the analysis. We were not able to vary k_2, k_5, and k_7 at all. Therefore, these eight parameters were fixed at previous values obtained via the simultaneous infrared and millimeter analysis which included transitions with $\Delta v_t \neq 0$ (5, 27). Values for the constants δ_K, c_1, c_2, c_3, H_{JK}, H_{KJ}, H_K, and h_K have been obtained for the first time. The use of the interaction constants c_1, c_2, and c_3 is necessary to reproduce the torsional state variation in the molecular asymmetry. The parameter δ_J, H_J, h_J, h_{JK}, and f_v were set at zero; their inclusion lowers the root-mean-square deviation of the fit only marginally.

The advantage of the IAM method is that the matrix elements off-diagonal in v_t do not play a significant role in the analysis. This advantage has been checked by simple elimination of the $\Delta v_t = \pm 1, \pm 2$ matrix elements from our analysis. The resulting root-mean-square deviation of the fit rises only to 1.7 MHz, although selected excited torsional state lines are fit much more poorly.

Our nonlinear least-squares fit to the microwave, millimeter, and submillimeter data with $J \leqslant 8$, $v_t \leqslant 2$ is significantly more accurate and coherent than previous nonphenomenological approaches (*5, 27*) which utilize pertubation theory and are not global in scope. However, we have not been able to fit the spectral lines to the normal ~100-kHz accuracy customary for most molecular rotation spectra. Given the nature of our technique, it is probable that the discrepancy between theory and experiment is due to shortcomings in the IAM Hamiltonian utilized and/or the exclusion of the $\hat{H}_{\text{dist}}$ matrix elements diagonal in K but off-diagonal in v_t. These matrix elements will be included in future work but it must be noted that, without the infrared data used by Lees and Baker (*5*), the constants multiplying most of the relevant terms (k_1–k_7) are not important to nor accurately determined by our analysis. It is unlikely that off-diagonal elements containing these constants will affect the present millimeter analysis significantly.

The phenomenological approach of Pickett *et al.* (*15*) to the analysis of ground torsional state spectra results in a fit that is significantly tighter than ours. These

TABLE III

Methanol *A* Transitions

VTOR	SIGMA	JU	KU	PU	<--	JL	KL	PL	FREQUENCY(MHZ)	RESIDUAL(MHZ)	REFERENCE
0	0	1	1	-	<--	1	0	+	303366.890	1.402	a
0	0	1	1	-	<--	1	1	+	834.267	0.299	b
0	0	1	0	+	<--	0	0	+	48372.456	0.078	c
1	0	1	0	+	<--	0	0	+	48257.490	0.019	d
2	0	1	0	+	<--	0	0	+	48192.120	-0.067	d
0	0	1	1	+	<--	0	0	+	350905.119	1.221	e,a
0	0	2	1	-	<--	2	0	+	304208.350	1.569	a
0	0	2	1	-	<--	2	1	+	2502.778	0.874	c
0	0	2	2	-	<--	2	1	+	484004.740	0.500	f
0	0	2	2	+	<--	2	1	-	481504.232	-0.384	f
1	0	2	1	-	<--	2	2	+	553763.582	-0.440	f
1	0	2	1	+	<--	2	2	-	554052.056	-0.596	f
0	0	2	0	+	<--	1	0	+	96741.420	0.205	g
0	0	2	1	+	<--	1	1	+	95914.290	-0.281	g
0	0	2	1	-	<--	1	1	-	97582.830	0.323	g
1	0	2	0	+	<--	1	0	+	96513.660	-0.360	g
1	0	2	1	+	<--	1	1	+	96396.010	-0.436	g
1	0	2	1	-	<--	1	1	-	96588.600	-0.145	g
2	0	2	0	+	<--	1	0	+	96383.130	-0.171	g
2	0	2	1	+	<--	1	1	+	96189.670	0.882	g
2	0	2	1	-	<--	1	1	-	96553.780	1.242	g
0	0	2	1	+	<--	1	0	+	398446.920	0.828	a
0	0	2	0	+	<--	1	1	+	-205791.270	-0.965	a
0	0	2	2	-	<--	1	1	-	579084.700	-0.143	f
1	0	2	2	+	<--	1	1	+	-457367.889	-0.132	f
1	0	2	2	-	<--	1	1	-	-457463.899	-0.174	f
0	0	3	1	-	<--	3	0	+	305473.520	1.724	a
0	0	3	1	-	<--	3	1	+	5005.321	1.531	c
0	0	3	2	-	<--	3	1	+	485263.263	0.809	f
0	0	3	2	+	<--	3	1	-	480269.321	-0.746	f
0	0	3	3	-	<--	3	2	+	251905.812	-2.266	e,a
0	0	3	3	+	<--	3	2	-	251917.050	-2.412	e,a
1	0	3	1	-	<--	3	2	+	553624.453	-0.288	f
1	0	3	1	+	<--	3	2	-	554202.988	0.442	f
0	0	3	0	+	<--	2	0	+	145103.230	0.258	g
0	0	3	1	+	<--	2	1	+	143865.790	-0.311	g
0	0	3	1	-	<--	2	1	-	146368.300	0.313	g
0	0	3	2	+	<--	2	2	+	145133.460	0.023	g
0	0	3	2	-	<--	2	2	-	145124.410	0.095	g
1	0	3	0	+	<--	2	0	+	144768.200	-0.525	g
1	0	3	1	+	<--	2	1	+	144589.820	-0.546	g
1	0	3	1	-	<--	2	1	-	144878.580	-0.234	g
1	0	3	2	+	<--	2	2	+	144728.700	-0.220	g
1	0	3	2	-	<--	2	2	-	144728.700	-0.946	g
2	0	3	0	+	<--	2	0	+	144571.970	-0.300	g
2	0	3	1	+	<--	2	1	+	144281.780	1.419	g
2	0	3	1	-	<--	2	1	-	144827.610	1.625	g
0	0	3	1	+	<--	2	0	+	445571.414	0.436	f
0	0	3	0	+	<--	2	1	+	-156602.420	-0.515	g
0	0	3	2	+	<--	2	1	+	629140.493	0.535	f
0	0	3	2	-	<--	2	1	-	626626.302	-0.349	f
0	0	3	1	-	<--	2	2	-	-335133.513	0.836	e
0	0	3	3	+	<--	2	2	+	397039.090	-2.407	a
0	0	3	3	-	<--	2	2	-	397041.410	-2.386	a
1	0	3	2	+	<--	2	1	+	-409035.534	-0.251	f
1	0	3	2	-	<--	2	1	-	-409323.292	-0.468	f
0	0	4	1	-	<--	4	0	+	307165.940	1.741	a
0	0	4	1	-	<--	4	1	+	8341.640	2.090	h
0	0	4	2	-	<--	4	1	+	486940.837	1.098	f
0	0	4	2	+	<--	4	1	-	478633.272	-1.124	f
0	0	4	3	-	<--	4	2	+	251866.579	-1.465	e,a
0	0	4	3	+	<--	4	2	-	251900.495	-1.625	e,a
0	0	4	4	-	<--	4	3	+	636420.231	6.028	e
0	0	4	4	+	<--	4	3	-	636420.231	6.158	e
1	0	4	1	-	<--	4	2	+	553437.476	-0.184	f
1	0	4	1	+	<--	4	2	-	554402.514	0.637	f
0	0	4	0	+	<--	3	0	+	193454.390	0.283	g
0	0	4	1	+	<--	3	1	+	191810.490	-0.260	g
0	0	4	1	-	<--	3	1	-	195146.760	0.250	g
0	0	4	2	-	<--	3	2	-	193488.030	-0.006	g
0	0	4	3	+	<--	3	3	+	193471.520	0.825	g
0	0	4	3	-	<--	3	3	-	193471.520	0.714	g
1	0	4	0	+	<--	3	0	+	193019.870	-0.796	g
1	0	4	1	+	<--	3	1	+	192778.520	-0.603	g
1	0	4	1	-	<--	3	1	-	193163.330	-0.389	g
1	0	4	2	+	<--	3	2	+	192963.470	-0.918	g
1	0	4	2	-	<--	3	2	-	192965.530	-0.674	g
1	0	4	3	+	<--	3	3	+	192963.470	0.539	g
1	0	4	3	-	<--	3	3	-	192963.470	0.537	g
2	0	4	0	+	<--	3	0	+	192757.650	-0.369	g
2	0	4	1	+	<--	3	1	+	192370.480	1.931	g
2	0	4	1	-	<--	3	1	-	193098.290	2.242	g
2	0	4	2	+	<--	3	2	+	192613.090	0.450	g
2	0	4	2	-	<--	3	2	-	192613.090	0.435	g

TABLE III—*Continued*

VTOR	SIGMA	JU	KU	PU	<--	JL	KL	PL	FREQUENCY(MHZ)	RESIDUAL(MHZ)	REFERENCE
2	0	4	3	+	<--	3	3	+	192739.440	-1.630	g
2	0	4	3	-	<--	3	3	-	192739.440	-1.630	g
0	0	4	1	+	<--	3	0	+	492278.713	-0.044	f
0	0	4	0	+	<--	3	1	+	-107013.850	0.049	g
0	0	4	2	+	<--	3	1	+	678785.455	0.759	f
0	0	4	2	-	<--	3	1	-	673745.931	-0.769	f
0	0	4	1	+	<--	3	2	+	-293463.990	-0.884	a
0	0	4	1	-	<--	3	2	-	-285111.150	1.004	a
0	0	4	2	+	<--	3	3	+	-58394.940	2.280	a
0	0	4	2	-	<--	3	3	-	-58429.010	2.434	a
1	0	4	2	+	<--	3	1	+	-360661.433	-0.172	f
1	0	4	2	-	<--	3	1	-	-361236.476	-1.042	f
0	0	5	1	-	<--	5	0	+	309290.400	1.571	a
0	0	5	1	-	<--	5	1	+	12511.000	2.002	i
0	0	5	2	-	<--	5	1	+	489036.955	1.199	f
0	0	5	2	+	<--	5	1	-	476605.142	-1.424	f
0	0	5	3	-	<--	5	2	+	251811.882	-0.484	e,a
0	0	5	3	+	<--	5	2	-	251890.901	-0.753	e,a
0	0	5	4	-	<--	5	3	+	636393.568	3.677	e
0	0	5	4	+	<--	5	3	-	636393.568	4.197	e
1	0	5	1	-	<--	5	2	+	553201.597	-0.005	f
1	0	5	1	+	<--	5	2	-	554651.031	0.839	f
0	0	5	0	+	<--	4	0	+	241791.430	0.345	e,a
0	0	5	1	+	<--	4	1	+	239746.250	-0.017	e,a
0	0	5	1	-	<--	4	1	-	243915.830	0.115	e,a
0	0	5	2	+	<--	4	2	+	241887.700	-0.185	e,a
0	0	5	2	-	<--	4	2	-	241842.320	0.037	e,a
0	0	5	3	+	<--	4	3	+	241832.950	1.133	e,a
0	0	5	3	-	<--	4	3	-	241832.950	0.743	e,a
0	0	5	4	+	<--	4	4	+	241806.510	-0.995	e,a
0	0	5	4	-	<--	4	4	-	241806.510	-0.994	e,a
1	0	5	0	+	<--	4	0	+	241267.880	-1.039	a
1	0	5	1	+	<--	4	1	+	240960.560	-0.437	a
1	0	5	1	-	<--	4	1	-	241441.240	-0.498	a
1	0	5	2	+	<--	4	2	+	241192.810	-0.613	a
1	0	5	2	-	<--	4	2	-	241196.350	-0.705	a
1	0	5	3	+	<--	4	3	+	241198.290	0.862	a
1	0	5	3	-	<--	4	3	-	241198.290	0.856	a
2	0	5	0	+	<--	4	0	+	240938.940	-0.538	a
2	0	5	1	+	<--	4	1	+	240454.850	2.627	a
2	0	5	1	-	<--	4	1	-	241364.120	2.523	a
2	0	5	2	+	<--	4	2	+	240757.910	0.716	a
2	0	5	2	-	<--	4	2	-	240757.910	0.686	a
2	0	5	3	+	<--	4	3	+	240916.160	-1.483	a
2	0	5	3	-	<--	4	3	-	240916.160	-1.483	a
0	0	5	1	+	<--	4	0	+	538570.582	-0.334	f
0	0	5	0	+	<--	4	1	+	-57032.920	0.644	a
0	0	5	2	+	<--	4	1	+	728862.523	0.693	f
0	0	5	2	-	<--	4	1	-	720441.236	-1.237	f
0	0	5	1	+	<--	4	2	+	-247228.693	-1.014	e,a
0	0	5	1	-	<--	4	2	-	-234683.390	1.085	e,a
1	0	5	2	+	<--	4	1	+	-312247.354	-0.393	f
1	0	5	2	-	<--	4	1	-	-313203.428	-1.330	f
0	0	6	1	-	<--	6	0	+	311852.640	0.985	e,a
0	0	6	1	-	<--	6	1	+	17513.341	1.578	c
0	0	6	2	-	<--	6	1	+	491550.827	0.818	f
0	0	6	2	+	<--	6	1	-	474196.319	-1.522	f
0	0	6	3	-	<--	6	2	+	251738.520	1.116	e,a
0	0	6	3	+	<--	6	2	-	251895.728	0.290	e,a
0	0	6	4	+	<--	6	3	-	636363.843	1.648	e
1	0	6	1	-	<--	6	2	+	552915.356	0.259	f
1	0	6	1	+	<--	6	2	-	554947.481	0.558	f
0	0	6	0	+	<--	5	0	+	290110.666	0.293	e,a
0	0	6	1	+	<--	5	1	+	287670.835	0.401	e,a
0	0	6	1	-	<--	5	1	-	292672.890	-0.309	a
0	0	6	2	+	<--	5	2	+	290264.150	-0.324	e,a
0	0	6	2	-	<--	5	2	-	290184.690	0.003	e,a
0	0	6	3	+	<--	5	3	+	290189.510	1.039	e,a
0	0	6	3	-	<--	5	3	-	290190.540	1.028	e,a
0	0	6	4	+	<--	5	4	+	290161.140	-1.195	e,a
0	0	6	4	-	<--	5	4	-	290161.140	-1.192	e,a
0	0	6	5	+	<--	5	5	+	290145.090	-1.378	e,a
0	0	6	5	-	<--	5	5	-	290145.090	-1.378	e,a
1	0	6	0	+	<--	5	0	+	289511.110	-1.453	a
1	0	6	1	+	<--	5	1	+	289134.050	-0.218	a
1	0	6	1	-	<--	5	1	-	289710.460	-0.688	a
1	0	6	2	+	<--	5	2	+	289414.030	-0.388	a
1	0	6	2	-	<--	5	2	-	289420.240	-0.533	a
1	0	6	3	+	<--	5	3	+	289429.750	1.984	a
1	0	6	3	-	<--	5	3	-	289429.750	1.967	a
2	0	6	0	+	<--	5	0	+	289114.820	-0.752	a
2	0	6	1	+	<--	5	1	+	288533.640	3.384	a
2	0	6	1	-	<--	5	1	-	289624.280	2.777	a
2	0	6	2	+	<--	5	2	+	288897.110	1.099	a
2	0	6	2	-	<--	5	2	-	288897.110	1.047	a

TABLE III—*Continued*

VTOR	SIGMA	JU	KU	PU	<--	JL	KL	PL	FREQUENCY(MHZ)	RESIDUAL(MHZ)	REFERENCE
2	0	6	3	+	<--	5	3	+	289087.370	-1.049	a
2	0	6	3	-	<--	5	3	-	289087.370	-1.049	a
0	0	6	1	+	<--	5	0	+	584449.713	-0.552	f
0	0	6	2	+	<--	5	1	+	779380.507	0.469	f
0	0	6	2	-	<--	5	1	-	766710.345	-1.100	f
0	0	6	1	+	<--	5	2	+	-201445.590	-0.460	a
0	0	6	1	-	<--	5	2	-	-183853.000	0.559	g
0	0	6	2	+	<--	5	3	+	38452.690	0.062	j
0	0	6	2	-	<--	5	3	-	38293.500	0.987	j
1	0	6	2	+	<--	5	1	+	-263793.856	-0.316	f
1	0	6	2	-	<--	5	1	-	-265224.400	-1.337	f
0	0	7	1	-	<--	7	0	+	314859.550	-0.171	a
0	0	7	1	-	<--	7	1	+	23347.530	0.335	j
0	0	7	2	-	<--	7	1	+	494481.683	-0.126	f
0	0	7	2	+	<--	7	1	-	471420.477	-1.350	f
0	0	7	3	-	<--	7	2	+	251641.667	2.754	e,a
0	0	7	3	+	<--	7	2	-	251923.631	1.406	e,a
0	0	7	4	-	<--	7	3	+	636337.419	-0.185	e
0	0	7	4	+	<--	7	3	-	636333.470	-0.249	e
1	0	7	1	+	<--	7	2	-	555291.142	-0.244	f
0	0	7	0	+	<--	6	0	+	338408.681	0.235	e,a
0	0	7	1	+	<--	6	1	+	335582.005	0.925	e,a
0	0	7	1	-	<--	6	1	-	341415.500	-1.012	e,a
0	0	7	2	+	<--	6	2	+	338639.939	-0.560	e,a
0	0	7	2	-	<--	6	2	-	338512.762	-0.118	e,a
0	0	7	3	+	<--	6	3	+	338540.795	1.128	e,a
0	0	7	3	-	<--	6	3	-	338543.204	1.196	e,a
0	0	7	4	+	<--	6	4	+	338512.762	-0.770	e,a
0	0	7	4	-	<--	6	4	-	338512.762	-0.758	e,a
0	0	7	5	+	<--	6	5	+	338486.337	-1.518	e,a
0	0	7	5	-	<--	6	5	-	338486.337	-1.518	e,a
0	0	7	1	+	<--	6	0	+	629921.337	0.365	f
0	0	7	0	+	<--	6	1	+	44069.490	0.936	g
0	0	7	2	+	<--	6	1	+	830349.412	-0.691	e,f
0	0	7	1	+	<--	6	2	+	-156127.700	0.824	g
0	0	7	1	-	<--	6	2	-	-132621.940	-0.206	g
0	0	7	3	+	<--	6	2	+	590277.688	2.178	e
0	0	7	2	+	<--	6	3	+	86903.060	-1.595	a
0	0	7	2	-	<--	6	3	-	86615.760	-0.121	a
1	0	7	2	+	<--	6	1	+	-215302.201	-0.157	f
1	0	7	2	-	<--	6	1	-	-217299.202	-0.921	f
0	0	8	1	-	<--	8	0	+	318318.793	-2.277	e,a
0	0	8	2	-	<--	8	1	+	497828.231	-1.984	f
0	0	8	2	+	<--	8	1	-	468293.771	-0.745	e,f
0	0	8	3	-	<--	8	2	+	251517.262	5.141	e,a
0	0	8	3	+	<--	8	2	-	251984.702	2.611	e,a
0	0	8	4	-	<--	8	3	+	636311.690	-2.018	e
0	0	8	4	+	<--	8	3	-	636304.355	-0.819	e
1	0	8	1	+	<--	8	2	-	555680.931	-1.852	f
0	0	8	0	+	<--	7	0	+	386681.920	0.125	a
0	0	8	1	+	<--	7	1	+	383477.880	1.795	a
0	0	8	1	-	<--	7	1	-	390141.730	-1.414	a
0	0	8	2	+	<--	7	2	+	387014.800	-1.032	a
0	0	8	2	-	<--	7	2	-	386824.430	-0.062	a
0	0	8	3	+	<--	7	3	+	386885.540	1.182	a
0	0	8	3	-	<--	7	3	-	386890.120	1.080	a
0	0	8	4	+	<--	7	4	+	386859.820	-0.675	a
0	0	8	4	-	<--	7	4	-	386859.820	-0.641	a
0	0	8	5	+	<--	7	5	+	386820.010	-1.682	a
0	0	8	5	-	<--	7	5	-	386820.010	-1.682	a
0	0	8	1	+	<--	7	0	+	674990.423	1.812	f
0	0	8	0	+	<--	7	1	+	95169.440	0.171	g
0	0	8	1	+	<--	7	2	+	-111289.620	3.318	g
0	0	8	1	-	<--	7	2	-	-80993.160	-1.690	a
0	0	8	3	+	<--	7	2	+	638523.486	4.117	e
0	0	8	3	-	<--	7	2	-	638817.830	2.663	e
0	0	8	2	+	<--	7	3	+	135376.760	-4.061	g
0	0	8	2	-	<--	7	3	-	134896.960	-1.405	g
0	0	8	3	+	<--	7	4	+	-249451.911	1.352	e,a
0	0	8	3	-	<--	7	4	-	-249443.402	1.260	e,a
1	0	8	2	+	<--	7	1	+	-166773.278	0.130	f
1	0	8	2	-	<--	7	1	-	-169427.231	0.175	f,g

a	Ref. 16	f	This work
b	Ref. 7	g	Ref. 5
c	Ref. 6	h	Ref. 27
d	Ref. 2	i	Ref. 4
e	Ref. 15	j	Ref. 1

authors varied 104 coefficients of polynomial power series to fit 270 lines involving $J \leqslant 20$ and $K \leqslant 6$ to a root-mean-square deviation of ~100 kHz. Their method involves a fraction of the computational effort involved in ours but is not quantum mechanical in origin.

Utilizing our determined parameters, and their uncertainties and correlations, we have predicted the frequencies and estimated uncertainties of all 2538 CH_3OH transitions involving $J \leqslant 10$ and $v_t \leqslant 2$. These predictions are available from the authors. Many of the predicted transitions lie at frequencies greater than 1 THz, and have not been studied at high accuracy in the laboratory. Of those predictions that can be compared with experimental measurements, the agreement is generally within 1–10 MHz. These lines were excluded from our data set because of their high values of J ($J = 9$ or 10), because we could not use error curve techniques to check assignments, or because error curve techniques showed the assignments to be ambiguous. In addition, Sastry *et al.* (*16*) have recently assigned a series of methanol lines in the range 101–114 GHz to the $K = -2 \leftarrow 1$, E, $v_t = 0$ Q-branch series. This $\Delta K = -3$ series was not included in our fit, but is well predicted by our analysis.

There are some serious disagreements between our predicted values and experimental assignments. Johnston and Srivastawa (*9*) and Johnston *et al.* (*10*) have published zero-field frequencies of the $K = 6 \leftarrow 5$, E, $v_t = 0$ Q-branch series obtained via laser Stark spectroscopy using the 337-μm HCN laser. These frequencies, accurate to 3–10 MHz, are not predicted well by our results. For example, the line at 890 445 MHz is assigned to the $J = 6$ transition, whereas our predicted value for this frequency is 890 304 MHz, with a predicted uncertainty of 15 MHz. In general, there are ⩾100-MHz discrepancies for the higher J members of this series. Since this represents a substantial extrapolation, this is not an unexpected result.

Sastry *et al.* (*16*) have assigned a series of lines from 25 to 40 GHz originally measured by Hughes *et al.* (*1*) to the $K = 9 \leftarrow 8$, $A\pm$, $v_t = 1$ Q-branch series. Our frequency predictions for the $J = 9$ and $J = 10$ lines of this series differ by 1.4 and 2.1 GHz from the experimental values with the assignments of Sastry *et al.* (*16*). If the theory is at fault, the above two sets of discrepancies are probably due to the fact that high-K transitions are involved, whereas these are noticeably deficient in our data set.

The final major discrepancy between prediction and experimental assignment involves a series of b-type P- and R-branch lines assigned by Sastry *et al.* (*16*) to $K = 2 \leftrightarrow 3$, E, $v_t = 1$ transitions. An example is the $J = 6 \leftarrow 7$, $K = 3 \leftarrow 2$ transition, predicted to lie at 22098 MHz, which is assigned to a line at 27227 MHz. Discrepancies of 5 GHz also exist between the $J = 5 \leftarrow 6$, $K = 3 \leftarrow 2$; $J = 8 \leftarrow 7$, $K = 2 \leftarrow 3$; $J = 9 \leftarrow 8$, $K = 2 \leftarrow 3$; and $J = 10 \leftarrow 9$, $K = 2 \leftarrow 3$ assignments and predictions. Again, this branch represents an extrapolation from the data set used in the analysis, and more work is needed to understand and resolve these discrepancies.

It must be reiterated, however, that our global treatment of the CH_3OH microwave, millimeter, and submillimeter data is capable of fitting almost 500 transitions of this species involving $v_t = 0, 1, 2$ and $J \leqslant 8$ to a root-mean-square deviation of ~1.2 MHz, and of predicting the great majority of transitions involving these

TABLE IV

Methanol *E* Transitions

VTOR	SIGMA	JU	KU	PU	<--	JL	KL	PL	FREQUENCY(MHZ)	RESIDUAL(MHZ)	REFERENCE
0	1	1	0	--	<--	1	-1	--	157270.700	-0.292	a
0	1	1	1	--	<--	1	0	--	165050.190	0.454	a
1	1	1	0	--	<--	1	1	--	189689.570	-0.799	a
0	1	1	0	--	<--	0	0	--	48377.090	0.219	b
1	1	1	0	--	<--	0	0	--	48247.890	0.202	b
2	1	1	0	--	<--	0	0	--	48178.000	0.005	b
0	1	1	-1	--	<--	0	0	--	-108893.940	0.182	a
1	1	1	1	--	<--	0	0	--	-141441.280	1.401	a
0	1	2	0	--	<--	2	-1	--	157276.040	-0.303	a
0	1	2	1	--	<--	2	0	--	165061.140	0.650	a
0	1	2	2	--	<--	2	1	--	24934.380	-0.308	c
0	1	2	-1	--	<--	1	-1	--	96739.390	0.235	a
0	1	2	0	--	<--	1	0	--	96744.580	0.074	a
0	1	2	1	--	<--	1	1	--	96755.510	0.251	a
1	1	2	-1	--	<--	1	-1	--	96501.660	0.188	a
1	1	2	0	--	<--	1	0	--	96493.590	-0.193	a
1	1	2	1	--	<--	1	1	--	96492.200	-0.225	a
2	1	2	-1	--	<--	1	-1	--	96391.090	-0.546	a
2	1	2	0	--	<--	1	0	--	96355.550	0.656	a
2	1	2	1	--	<--	1	1	--	96334.990	0.315	a
0	1	2	-2	--	<--	1	-1	--	520179.066	2.053	d
0	1	2	0	--	<--	1	-1	--	254015.340	-0.158	e
0	1	2	-1	--	<--	1	0	--	-60531.420	0.417	e
0	1	2	1	--	<--	1	0	--	261805.710	0.714	e
0	1	2	0	--	<--	1	1	--	-68305.630	-0.400	e
0	1	2	2	--	<--	1	1	--	121689.850	-0.097	a
1	1	2	1	--	<--	1	0	--	-93196.710	1.235	a
0	1	3	-2	--	<--	3	-1	--	423468.663	1.438	f
0	1	3	0	--	<--	3	-1	--	157272.470	-0.407	a
0	1	3	1	--	<--	3	0	--	165099.310	0.956	a
0	1	3	2	--	<--	3	1	--	24928.700	-0.563	c
0	1	3	3	--	<--	3	2	--	530647.277	1.633	f
1	1	3	0	--	<--	3	1	--	189692.150	-1.464	a
0	1	3	-2	--	<--	2	-2	--	145126.370	-0.135	a
0	1	3	-1	--	<--	2	-1	--	145097.470	0.333	a
0	1	3	0	--	<--	2	0	--	145093.750	0.078	a
0	1	3	1	--	<--	2	1	--	145131.880	0.344	a
0	1	3	2	--	<--	2	2	--	145126.370	0.258	a
1	1	3	-2	--	<--	2	-2	--	144728.700	-0.774	a
1	1	3	-1	--	<--	2	-1	--	144750.200	0.283	a
1	1	3	0	--	<--	2	0	--	144736.300	-0.389	a
1	1	3	1	--	<--	2	1	--	144734.520	-0.282	a
1	1	3	2	--	<--	2	2	--	144733.320	-1.225	a
2	1	3	-1	--	<--	2	-1	--	144583.910	-0.855	a
2	1	3	0	--	<--	2	0	--	144530.560	0.959	a
2	1	3	1	--	<--	2	1	--	144499.760	0.542	a
2	1	3	2	--	<--	2	2	--	144579.860	-1.251	a
0	1	3	-2	--	<--	2	-1	--	568566.054	1.692	d
0	1	3	0	--	<--	2	-1	--	302369.900	-0.115	e
0	1	3	-1	--	<--	2	0	--	-12178.600	0.606	g
0	1	3	1	--	<--	2	0	--	310193.000	0.974	e
0	1	3	0	--	<--	2	1	--	-19967.300	-0.482	c
0	1	3	2	--	<--	2	1	--	170060.630	-0.169	a
0	1	3	1	--	<--	2	2	--	120197.520	0.672	a
0	1	3	3	--	<--	2	2	--	675773.439	1.683	d
1	1	3	1	--	<--	2	0	--	-44955.810	1.115	a
1	1	3	0	--	<--	2	1	--	334426.590	-1.826	d
0	1	4	-4	--	<--	4	-3	--	524947.234	-3.391	d
0	1	4	-2	--	<--	4	-1	--	423538.258	0.839	f
0	1	4	0	--	<--	4	-1	--	157246.100	-0.726	a
0	1	4	1	--	<--	4	0	--	165190.530	1.145	a
0	1	4	2	--	<--	4	1	--	24933.470	-0.823	c
0	1	4	3	--	<--	4	2	--	530610.288	0.991	f
1	1	4	0	--	<--	4	1	--	189694.390	-1.459	a
0	1	4	-3	--	<--	3	-3	--	193488.990	-0.211	a
0	1	4	-2	--	<--	3	-2	--	193511.210	-0.195	a
0	1	4	-1	--	<--	3	-1	--	193441.620	0.409	a
0	1	4	0	--	<--	3	0	--	193415.370	0.211	a
0	1	4	1	--	<--	3	1	--	193506.600	0.410	a
0	1	4	2	--	<--	3	2	--	193511.210	-0.010	a
0	1	4	3	--	<--	3	3	--	193474.330	-0.543	a
1	1	4	-3	--	<--	3	-3	--	192952.700	-1.369	a
1	1	4	-2	--	<--	3	-2	--	192962.100	-0.879	a
1	1	4	-1	--	<--	3	-1	--	192996.030	0.418	a
1	1	4	0	--	<--	3	0	--	192974.360	-0.453	a
1	1	4	1	--	<--	3	1	--	192972.080	-0.499	a
1	1	4	2	--	<--	3	2	--	192973.650	-1.710	a
1	1	4	3	--	<--	3	3	--	192957.680	1.877	a
2	1	4	-2	--	<--	3	-2	--	192756.310	3.036	a
2	1	4	-1	--	<--	3	-1	--	192773.580	-1.089	a
2	1	4	0	--	<--	3	0	--	192702.240	1.222	a
2	1	4	1	--	<--	3	1	--	192661.130	0.721	a
2	1	4	2	--	<--	3	2	--	192768.140	-1.528	a

TABLE IV—*Continued*

VTOR	SIGMA	JU	KU	PU	<--	JL	KL	PL	FREQUENCY(MHZ)	RESIDUAL(MHZ)	REFERENCE
0	1	4	-1	--	<--	3	-2	--	-230027.060	-1.046	e
0	1	4	-2	--	<--	3	-1	--	616979.984	1.354	d
0	1	4	0	--	<--	3	-1	--	350687.730	-0.307	e
0	1	4	-1	--	<--	3	0	--	36169.240	0.907	c
0	1	4	1	--	<--	3	0	--	358605.800	1.256	e
0	1	4	0	--	<--	3	1	--	28316.030	-0.775	c
0	1	4	2	--	<--	3	1	--	218440.050	-0.433	e
0	1	4	1	--	<--	3	2	--	168577.860	0.934	e
0	1	4	3	--	<--	3	2	--	724121.576	1.059	d
0	1	4	2	--	<--	3	3	--	-337135.873	-1.449	d
1	1	4	0	--	<--	3	1	--	382666.474	-1.953	d
0	1	5	-4	--	<--	5	-3	--	524908.133	-1.734	d
0	1	5	-2	--	<--	5	-1	--	423675.155	0.070	f
0	1	5	0	--	<--	5	-1	--	157178.970	-0.948	a
0	1	5	1	--	<--	5	0	--	165369.440	1.222	a
0	1	5	2	--	<--	5	1	--	24959.080	-1.033	c
0	1	5	3	--	<--	5	2	--	530549.271	0.299	f
1	1	5	0	--	<--	5	1	--	189696.750	-1.440	a
0	1	5	-4	--	<--	4	-4	--	241813.257	1.290	f,e
0	1	5	-3	--	<--	4	-3	--	241852.352	-0.373	f,e
0	1	5	-2	--	<--	4	-2	--	241904.119	-0.296	f,e
0	1	5	-1	--	<--	4	-1	--	241767.224	0.474	f,e
0	1	5	0	--	<--	4	0	--	241700.219	0.378	f,e
0	1	5	1	--	<--	4	1	--	241879.073	0.398	f,e
0	1	5	2	--	<--	4	2	--	241904.407	-0.088	f,e
0	1	5	3	--	<--	4	3	--	241843.646	-0.523	f,e
0	1	5	4	--	<--	4	4	--	241829.646	-0.667	f,e
1	1	5	-3	--	<--	4	-3	--	241179.900	-1.243	e
1	1	5	-2	--	<--	4	-2	--	241187.400	-0.810	e
1	1	5	-1	--	<--	4	-1	--	241238.160	0.518	e
1	1	5	0	--	<--	4	0	--	241205.990	-0.572	e
1	1	5	1	--	<--	4	1	--	241203.690	-0.531	e
1	1	5	2	--	<--	4	2	--	241210.680	-2.038	e
1	1	5	3	--	<--	4	3	--	241166.530	1.464	e
2	1	5	-2	--	<--	4	-2	--	240936.730	3.925	e
2	1	5	-1	--	<--	4	-1	--	240958.800	-1.470	e
2	1	5	0	--	<--	4	0	--	240869.490	1.441	e
2	1	5	1	--	<--	4	1	--	240817.940	0.811	e
2	1	5	2	--	<--	4	2	--	240952.070	-1.744	e
0	1	5	-3	--	<--	4	-4	--	-283094.900	3.000	e
0	1	5	-1	--	<--	4	-2	--	-181771.050	-0.380	a
0	1	5	-2	--	<--	4	-1	--	665442.450	0.615	d
0	1	5	0	--	<--	4	-1	--	398946.230	-0.437	d
0	1	5	-1	--	<--	4	0	--	84521.210	1.286	h
0	1	5	1	--	<--	4	0	--	407069.553	1.493	d
0	1	5	2	--	<--	4	1	--	266838.130	-0.658	e
0	1	5	1	--	<--	4	2	--	216945.600	1.219	e
0	1	5	3	--	<--	4	2	--	772453.803	0.336	d
0	1	5	2	--	<--	4	3	--	-288705.567	-0.764	f,e
1	1	5	1	--	<--	4	0	--	51509.280	0.908	e
1	1	5	0	--	<--	4	1	--	430900.319	-2.092	d
0	1	6	-4	--	<--	6	-3	--	524860.820	0.350	d
0	1	6	-2	--	<--	6	-1	--	423912.696	-0.922	f
0	1	6	0	--	<--	6	-1	--	157048.620	-0.937	a
0	1	6	1	--	<--	6	0	--	165678.770	0.905	a
0	1	6	2	--	<--	6	1	--	25018.140	-1.113	c
0	1	6	3	--	<--	6	2	--	530454.695	-0.556	f
0	1	6	-5	--	<--	5	-5	--	290117.815	-1.750	f,e
0	1	6	-4	--	<--	5	-4	--	290162.430	1.430	f,e
0	1	6	-3	--	<--	5	-3	--	290209.700	-0.697	f,e
0	1	6	-2	--	<--	5	-2	--	290307.563	-0.119	f,e
0	1	6	-1	--	<--	5	-1	--	290069.824	0.675	f,e
0	1	6	0	--	<--	5	0	--	289939.477	0.689	f,e
0	1	6	1	--	<--	5	1	--	290248.762	0.328	f,e
0	1	6	2	--	<--	5	2	--	290307.563	-0.011	f,e
0	1	6	3	--	<--	5	3	--	290213.238	-0.615	f,e
0	1	6	4	--	<--	5	4	--	290183.210	-1.114	f,e
0	1	6	5	--	<--	5	5	--	290138.890	1.662	f,e
1	1	6	-3	--	<--	5	-3	--	289399.590	-0.998	e
1	1	6	-2	--	<--	5	-2	--	289402.490	-0.608	e
1	1	6	-1	--	<--	5	-1	--	289475.610	0.521	e
1	1	6	0	--	<--	5	0	--	289429.120	-1.221	e
1	1	6	1	--	<--	5	1	--	289427.600	-0.594	e
1	1	6	2	--	<--	5	2	--	289443.930	-1.825	e
1	1	6	3	--	<--	5	3	--	289355.020	0.481	e
2	1	6	-2	--	<--	5	-2	--	289111.350	4.871	e
2	1	6	-1	--	<--	5	-1	--	289138.820	-1.675	e
2	1	6	0	--	<--	5	0	--	289031.290	1.691	e
2	1	6	1	--	<--	5	1	--	288969.290	1.029	e
2	1	6	2	--	<--	5	2	--	289130.620	-1.826	e
0	1	6	-3	--	<--	5	-4	--	-234698.450	1.020	e
0	1	6	-1	--	<--	5	-2	--	-133605.500	0.436	a
0	1	6	-2	--	<--	5	-1	--	713982.470	-0.297	f

TABLE IV—*Continued*

VTOR	SIGMA	JU	KU	PU	<--	JL	KL	PL	FREQUENCY(MHZ)	RESIDUAL(MHZ)	REFERENCE
0	1	6	-1	--	<--	5	0	--	132890.790	1.559	a
0	1	6	1	--	<--	5	0	--	455618.116	1.463	d
0	1	6	0	--	<--	5	1	--	124569.970	-0.600	a
0	1	6	2	--	<--	5	1	--	315266.830	-0.857	e
0	1	6	1	--	<--	5	2	--	265289.650	1.329	e
0	1	6	3	--	<--	5	2	--	820762.501	-0.324	d
0	1	6	2	--	<--	5	3	--	-240241.502	-0.104	f,e
1	1	6	1	--	<--	5	0	--	99730.900	0.896	a
1	1	6	0	--	<--	5	1	--	479126.480	-2.051	d
0	1	7	-4	--	<--	7	-3	--	524804.969	2.800	d
0	1	7	0	--	<--	7	-1	--	156828.520	-0.647	a
0	1	7	1	--	<--	7	0	--	166169.210	-0.093	a
0	1	7	2	--	<--	7	1	--	25124.880	-1.045	c
0	1	7	3	--	<--	7	2	--	530316.196	-1.502	f
0	1	7	-5	--	<--	6	-5	--	338456.499	-1.536	f,e
0	1	7	-4	--	<--	6	-4	--	338504.099	1.355	f,e
0	1	7	-3	--	<--	6	-3	--	338559.928	-1.118	f,e
0	1	7	-2	--	<--	6	-2	--	338722.940	-0.564	f,e
0	1	7	-1	--	<--	6	-1	--	338344.628	0.793	f,e
0	1	7	0	--	<--	6	0	--	338124.502	1.057	f,e
0	1	7	1	--	<--	6	1	--	338614.999	0.115	f,e
0	1	7	2	--	<--	6	2	--	338721.630	0.074	f,e
0	1	7	3	--	<--	6	3	--	338583.195	-0.808	f,e
0	1	7	4	--	<--	6	4	--	338530.249	-1.511	f,e
0	1	7	5	--	<--	6	5	--	338475.290	1.441	f,e
0	1	7	-3	--	<--	6	-4	--	-186300.950	-1.526	a
0	1	7	-1	--	<--	6	-2	--	-85567.970	1.813	e
0	1	7	-2	--	<--	6	-1	--	762635.948	-1.174	d
0	1	7	-1	--	<--	6	0	--	181296.030	1.752	a
0	1	7	1	--	<--	6	0	--	504293.685	0.936	d
0	1	7	0	--	<--	6	1	--	172445.950	0.369	a
0	1	7	2	--	<--	6	1	--	363739.820	-0.989	e
0	1	7	1	--	<--	6	2	--	313596.840	1.209	e
0	1	7	3	--	<--	6	2	--	869037.809	-1.444	d
0	1	7	2	--	<--	6	3	--	-191733.050	0.645	a
1	1	7	1	--	<--	6	0	--	147943.630	1.002	a
1	1	7	0	--	<--	6	1	--	527342.624	-2.271	d
0	1	8	-4	--	<--	8	-3	--	524740.167	5.510	d
0	1	8	-2	--	<--	8	-1	--	424857.263	-4.168	f
0	1	8	0	--	<--	8	-1	--	156488.950	0.176	a
0	1	8	1	--	<--	8	0	--	166898.650	-2.147	e
0	1	8	2	--	<--	8	1	--	25294.410	-0.765	c
0	1	8	3	--	<--	8	2	--	530123.294	-2.459	f
1	1	8	0	--	<--	8	1	--	189700.490	-2.054	a
0	1	8	-5	--	<--	7	-5	--	386788.660	-1.021	e
0	1	8	-4	--	<--	7	-4	--	386837.700	1.713	e
0	1	8	-3	--	<--	7	-3	--	386901.950	-1.549	e
0	1	8	-2	--	<--	7	-2	--	387153.550	-0.884	e
0	1	8	-1	--	<--	7	-1	--	386587.270	0.979	e
0	1	8	0	--	<--	7	0	--	386247.660	1.763	e
0	1	8	1	--	<--	7	1	--	386977.140	-0.250	e
0	1	8	2	--	<--	7	2	--	387146.560	-0.080	e
0	1	8	3	--	<--	7	3	--	386953.820	-0.876	e
0	1	8	4	--	<--	7	4	--	386869.410	-2.114	e
0	1	8	5	--	<--	7	5	--	386802.300	0.869	e
0	1	8	-3	--	<--	7	-4	--	-137903.060	-4.391	a
0	1	8	-1	--	<--	7	-2	--	-37703.720	3.276	c
0	1	8	-2	--	<--	7	-1	--	811445.210	-2.511	d
0	1	8	-1	--	<--	7	0	--	229758.760	1.637	e
0	1	8	1	--	<--	7	0	--	553146.296	-0.398	d
0	1	8	2	--	<--	7	3	--	-143169.500	1.557	a
1	1	8	1	--	<--	7	0	--	196146.210	1.138	a
1	1	8	0	--	<--	7	1	--	575547.119	-2.427	d

a	Ref. 5	e	Ref. 16
b	Ref. 2	f	Ref. 15
c	Ref. 1	g	Ref. 4
d	This work	h	Ref. 8

torsional quantum numbers and $J \leqslant 10$ to 1–10 MHz. Predicted frequencies should be of use to radioastronomers, especially for excited torsional states not treated by Pickett *et al.* (15). Future work will be in the direction of improving our analysis and including higher *J*, *K* data in the fit.

TABLE V

Rotation, Torsion, Distortion, and Interaction Constants of CH_3OH

Constant (MHz unless noted)	Present Value [a]	Other Values [b]
A	127630.7538(1583)	127597[c],127603[d]
B	24684.1785(2751)	24676.6[c], 24629[d]
C	23765.3680(2738)	23772.8[c], 23761
D_{ab}	-77.6655(4671)	-78.2(5.0)
$F(cm^{-1})$	27.63354173(3533)	27.6266[c]
ρ(unitless)	0.8097451117(1452)	0.809739[c]
$V_3(cm^{-1})$	373.0839507(9174)	373.10(9)
$V_6(cm^{-1})$	-0.80(fixed)	-0.80(12)
F_v	-71.43105(2521)	-71.637(50)
G_v	-3.535184(2482)	-3.5012(27)
$L_v x10^2$	4.01084(30762)	6.78(51)
$D_J x10^2$	4.9768(284)	4.92(20)
$D_{JK} x10^1$	2.86082(3103)	2.864(58)
D_K	1.058349(23160)	1.27(6)
k_1	-3.8(fixed)	-3.8(1.1)
k_2	-80.0(fixed)	-80(3)
k_3	-132.0(fixed)	-132(4)
k_4	-249.0(fixed)	-249(7)
k_5	161.0(fixed)	161(23)
k_6	884.0(fixed)	884(4000)
k_7	0.0(fixed)	0(fixed)
δ_J	0.0(fixed)	
δ_K	-0.75071(11932)	
c_1	-1.22722(9944)	
c_2	1.1392(2378)	
$c_3 x10^2$	-1.4695(6582)	
H_J	0.0(fixed)	
$H_{JK} x10^4$	-2.8164(4998)	
$H_{KJ} x10^4$	9.42500(1.66993)	
$H_K x10^2$	-1.071236(92898)	
h_J	0.0(fixed)	
h_{JK}	0.0(fixed)	
$h_K x10^2$	-5.92119(87581)	
f_v	0.0(fixed)	

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

[b] References (5) and (27) unless otherwise noted.

[c] Taken from combinations of constants of references (5) and (27).

[d] Reference (2).

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