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IDENTIFICATION OF INTERSTELLAR METHANOL LINES

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ABSTRACT

The extended internal axis method Hamiltonian of Herbst *et al.* has been employed to study the rotational spectrum of methanol out to high values of the rotational quantum number J. For $^{12}CH_3OH$ the available laboratory data, consisting of 783 lines out to $J = 22$, have been fitted with a Hamiltonian containing 32 free parameters. For $^{13}CH_3OH$ a Hamiltonian with 23 free parameters is sufficient for fitting 455 lines, also out to $J = 22$. Frequency predictions based on these fits have permitted the identification of a number of previously unidentified interstellar lines from OMC-1. The majority of these are b-type R-branch transitions of $^{12}CH_3OH$. The observed line strengths are consistent with a rotational temperature for methanol of 146.2 ± 2.7 K and column densities of $3.26 \pm 0.14\ 10^{16}\ \mathrm{cm^{-2}}$ (for $^{12}CH_3OH$) and $1.88 \pm 0.27\ 10^{15}\ \mathrm{cm^{-2}}$ (for $^{13}CH_3OH$).

The quantum number limit of $J = 22$ in these fits corresponds roughly, in excitation energy, with the most highly excited lines presently detectable from hot interstellar clouds such as Orion. It is now practical to make frequency predictions with uncertainties of 10 MHz or less for the great majority of methanol lines of astrophysical interest.

Subject headings: interstellar: molecules — line identifications — molecular processes

I. INTRODUCTION

Frequently in the study of interstellar molecules the measurement and assignment of molecular transitions in the laboratory has lagged behind their astronomical detection. In some cases this has been due to the special conditions of interstellar chemistry, which lead to the production of certain rare molecular species which may be difficult to study in the laboratory. In other cases it is due to theoretical difficulties in analyzing the laboratory data and in predicting accurate transition frequencies. Methanol is an abundant interstellar molecule. It is not an "exotic" special product of interstellar chemistry nor is it in any way difficult to obtain and study in the laboratory. Yet the problem of obtaining accurate frequency predictions most assuredly has been present. Since the first detection by Ball *et al.* (1970), over 200 interstellar lines of methanol have been observed. But throughout this period it has not been possible to obtain *a priori* frequencies for a large fraction of the transitions of methanol. Indeed these frequencies have been so poorly known that methanol has proved a considerable annoyance to radio astronomers, with strong lines cropping up in unexpected places throughout the spectum.

Molecular spectroscopists have not been neglectful of their duty. Starting with such early work as that of Hughes, Good, and Coles (1951) and Burkhard and Dennison (1951), there has been a long history of major steady progress in the understanding of methanol (see, e.g., Lees and Baker 1968; Sastry *et al.* 1984; Herbst *et al.*, 1984). The time span involved simply reflects the difficulty of the subject. The problem is caused by the internal (torsional) motion in the molecule. Two techniques have been developed to analyze rotational-torsional spectra. The first, the principal axis method (PAM) is essentially a perturbation theory approach to the torsional interactions. It is a relatively straightforward technique which is appropriate to cases where torsional effects are fairly modest. The alternate, internal axis method (IAM) has the advantage of removing the strong coupling between torsion and rotation through its choice of coordinate systems and is the method of choice for methanol where torsional effects are large. It unfortunately adds considerable computational complexity. The internal axis method has proved essential in the study of a number of additional internal rotor systems including methyl mercaptan, acetaldehyde, and to a lesser degree methyl formate (Sastry *et al.* 1986; Liang *et al.* 1986; Plummer, Herbst, and De Lucia 1987).

This current work is motivated by our desire to sort out the currently unexplained features in the interstellar spectrum of methanol. Sutton *et al.* (1985) reported 10 strong lines from OMC 1 which were present in the laboratory spectrum of an isotopically mixed sample of methanol but for which quantum numbers were not assigned. An additional 12 such lines were given by Blake *et al.* (1986). Clearly it is desirable to obtain assignments for these lines. Of equal importance for future progress in millimeter astronomy would be the ability to predict methanol frequencies to sufficient accuracy (~1 MHz) to make astronomical assignments. This is a formidable computing task, requiring the use of supercomputer technology. The IAM calculation requires the diagonalization of a large rotational-torsional Hamiltonian matrix. To cover those energy levels excited under interstellar conditions, this calculation must extend out to fairly high quantum numbers ($J \sim 20$–25). In this paper we report the results of such calculations, carried out on a Cray X-MP/14. Calculations were done for both $^{12}CH_3OH$ and $^{13}CH_3OH$ isotopic species. We are able to provide plausible assignments for all of the unassigned methanol transitions in Sutton *et al.* (1985) and Blake *et al.* (1986). In addition we have searched the list of unidentified microwave and millimeter-wave lines contaned in Lovas (1986). Other than two lines of $^{13}CH_3OH$ which have since been measured in the laboratory, we can only attribute one additional line from this list as being due to methanol.

II. THEORETICAL TREATMENT

a) Spectral Designations

The threefold symmetric torsional barrier in methanol leads to the existence of three torsional symmetry states, designated A, $E1$, and $E2$. For the E species, states of $E1$ symmetry with a component of angular momentum K along the symmetry axis are degenerate with those of $E2$ having a component $-K$. Thus it is simplest to refer to these states as doubly degenerate states of E symmetry where K can run over positive and negative values (Lees 1973*a*). Levels of the A species are also doubly degenerate (except for $K = 0$), but this degeneracy is broken by the slight asymmetry of the molecule. Following Lees and Baker (1968) we designate the members of these doublets by the notation $A+$ and $A-$. This splitting is analogous to the K doubling which occurs in a rigid asymmetric top. An alternate convention for labeling the A symmetry states would be to use the standard asymmetric top notation $J_{k_a k_c}$ as is done by Kuriyama *et al.* (1986). However we have preferred to stick to the former notation, which has been in more general use in the laboratory spectroscopy of methanol and in radio astronomy. It is important to note that this molecular asymmetry does *not* break the degeneracy in the E species between $E1(K)$ and $E2(-K)$.

b) Selection Rules

A variety of allowed transitions are possible in methanol due to the presence of significant dipole moments along both the a and b axes ($\mu_a = 0.896\ D$, $\mu_b = 1.412\ D$; Sastry, Lees, and Van der Linde 1981). Selection rules for strongly allowed Q-branch transitions are

$$\Delta J = 0 \quad \Delta K = \pm 1 \qquad\qquad (E \text{ species})$$
$$\Delta J = 0 \quad \Delta K = 0, \pm 1 \quad \pm \leftrightarrow \mp \quad (A \text{ species})\,.$$

The A species K-doubling transitions ($\Delta K = 0$) occur at fairly low frequencies (<10 GHz). The remaining b-type Q-branch transitions occur in tight bands, many of them at infrared frequencies ($\nu > 1000$ GHz). Selection rules for P and R branch transitions are

$$\Delta J = \pm 1 \quad \Delta K = 0, \pm 1 \qquad\qquad (E \text{ species})$$
$$\Delta J = \pm 1 \quad \Delta K = 0, \pm 1 \quad \pm \leftrightarrow \pm \quad (A \text{ species})\,.$$

The a-type ($\Delta K = 0$) R branch transitions also occur in bands, although the $K = 1$ $A \pm$ members are split off from the centers of these bands by as much as several GHz by the molecular asymmetry. The b-type ($\Delta K = \pm 1$) P and R branch transitions appear as isolated lines in the spectrum. These lines form series within which lines are spaced at intervals of approximately 48 GHz. Description of transitions as a-type or b-type is an idealization in the IAM axis system, since $\Delta K = \pm 1$ matrix elements mix even and odd K basis functions to a small degree.

c) Rotational-Torsional Hamiltonian

This work is based on the IAM rotational-torsional Hamiltonian of Herbst *et al.* (1984). Torsional eigenfunctions, characterized by quantum numbers $v_t = 0, 1, 2, \ldots$ and $\sigma = 1$ ($E1$), 0 (A), and -1 ($E2$), are first calculated as linear combinations of free rotor states by diagonalizing the torsional Hamiltonian. Subsequently the total Hamiltonian, including rotational, distortional, and interaction terms is diagonalized to yield overall energies and eigenstates. The Hamiltonian of Herbst *et al.* contains 34 parameters including ordinary rotational constants ($A, B, C, D_J, \ldots$), parameters describing the size of the torsional potential (e.g., V_3), and numerous interaction terms. In their fit to rotational lines up to $J = 8$ they found it necessary to vary only 21 of these parameters to obtain adequate agreement with the data. In extending this fitting procedure up to much higher quantum numbers ($J \sim 22$) it is necessary to include the majority of the remaining parameters.

Recently Nakagawa, Tsunekawa, and Kojima (1987) have described a generalized fourth-order effective Hamiltonian for methanol in which indeterminate terms have been removed through full application of the symmetry properties of the molecule. The problem of indeterminacy in classical internal axis method analyses is well known and is discussed by Lees and Baker (1968) and Lees (1970, 1973*b*). The approach of Nakagawa *et al.* has the further advantage of including certain off-diagonal matrix elements omitted by Herbst *et al.* (1984) and by this work. In reanalyzing the $J \leq 8$ data of Herbst *et al.*, Nakagawa *et al.* were able to reduce the RMS error of the fit by about a factor of 2, demonstrating the power of their technique. However, in analyzing data for large quantum numbers it is important to include higher order terms in the Hamiltonian. In particular we find that a number of sixth-order terms, such as the centrifugal distortion terms H_{JK}, H_{KJ}, H_K, h_J, h_{JK}, and h_K, are critical in obtaining adequate agreement with the data out to $J = 22$. The present limitation of Nakagawa's technique to fourth order is a serious drawback in using it to fit the higher J data.

d) Fits to $^{12}CH_3OH$ Data

The data set used for fitting the spectrum of $^{12}CH_3OH$ starts with the 470 transitions with $J \leq 8$ and $v_t \leq 2$ listed in Herbst *et al.* (1984). To these were added various transitions with quantum numbers in the range $8 < J \leq 22$. Most of these frequencies were taken from Lees and Baker (1968) and Sastry, Lees, and De Lucia (1984) with additional data from Lees *et al.* (1973), Johnston, Srivastava, and Lees (1980), Pickett *et al.* (1981), from recent laboratory measurements at Duke, and from the astronomical data. Specifically excluded was the $v_t = 1$ $K = 9$–8 A species Q branch assigned by Sastry, Lees, and De Lucia (1984) which could not be adequately fitted. Other bands which were *not* well predicted by Herbst *et al.* *are* successfully included in this analysis. Among these are the $v_t = 0$ $K = 6$–5 E species Q branch of Johnston *et al.* and $v_t = 1$ $K = 2$–3 E species b-type lines from Sastry, Lees, and De Lucia (1984). In all a total of 783 transitions out to $J = 22$ are included in the present analysis. These data are fitted by the Hamiltonian with 32 adjustable parameters to an RMS deviation of 4.40 MHz. The derived spectroscopic constants are listed in Table 1. The majority of these constants are in good agreement with the values previously determined by Herbst *et al.* (1984). A few are significantly different. For example, the value of A differs by over 100 MHz from the value previously reported. In this case the value of A is found to be strongly correlated with parameters previously held fixed, specifically the Kirtman interaction constants k_2 and k_5. The difference in A is largely compensated by the changes in k_2 and k_5. Transition frequencies calculated using the new constants agree quite closely with those calculated by Herbst *et al.* for the

TABLE 1

SPECTROSCOPIC CONSTANTS FOR $^{12}CH_3OH$

Constant (MHz unless noted)	Current Value	Herbst *et al.* 1984
A	127511.6(1.8)	127630.7538(1583)
B	24687.04(32)	24684.1785(2751)
C	23762.76(32)	23765.3680(2738)
D_{ab}	−79.0(8)	−77.6655(4671)
F (cm^{-1})	27.6576(6)	27.63354173(3533)
ρ (dimensionless)	0.81010(31)	0.8097451117(1452)
V_3 (cm^{-1})	373.859(25)	373.0839507(9174)
F_v	−71.49(8)	−71.43105(2521)
G_v	−3.574(6)	−3.535184(2482)
L_v	−0.070(4)	0.0401084(30762)
D_{JK}	0.2774(17)	0.286082(3103)
D_J	0.05094(22)	0.049768(284)
D_K	1.179(11)	1.058349(23160)
k_1	−0.05(7)	−3.8 (fixed)
k_2	−58.93(35)	−80.0 (fixed)
k_3	−172.8(4)	−132.0 (fixed)
k_4	−270.8(2.1)	−249.0 (fixed)
k_5	345.4(3.0)	161.0 (fixed)
k_6	180.(500.)	884.0 (fixed)
k_7	0.0 (fixed)	0.0 (fixed)
δ_J	0.00136(12)	0.0 (fixed)
δ_K	−0.141(20)	−0.75071(11932)
c_1	−1.74(5)	−1.22722(9944)
c_2	0.6(5)	1.1392(2378)
V_6 (cm^{-1})	−1.55(6)	−0.80 (fixed)
H_J	0.0 (fixed)	0.0 (fixed)
H_{JK}	−0.000070(6)	−0.00028164(4998)
H_{KJ}	−0.00015(4)	0.000942500(166993)
H_K	0.00048(17)	−0.01071236(92898)
h_J	−0.00000142(14)	0.0 (fixed)
h_{JK}	0.00018(5)	0.0 (fixed)
h_K	−0.0140(7)	−0.0592119(87581)
f_v	0.00205(35)	0.0 (fixed)
c_3	0.0104(22)	−0.014695(6582)

NOTE.—Figures in parentheses represent 1 σ uncertainties in the least significant digits.

smaller values of the quantum numbers J, K, and v_t. Differences become apparent particularly in the higher J transitions. For the $J \le 8$ data set of Herbst *et al.* the two sets of predictions differ by at most 12 MHz (a $v_t = 2$ line predicted rather poorly by each calculation) and generally agree within 1–2 MHz.

The available data well constrain the ground torsional state and to a somewhat lesser degree the first torsionally excited state. R branch a-type data are available only to $J = 8$. But some b-type lines are identified out to very high J, in some cases well past $J = 22$. These b-type lines provide the principal constraints on those parameters held fixed by Herbst *et al.* but varied in this work: the Kirtman constants $k_1 \rightarrow k_6$, the second harmonic term in the torsional potential (V_6), and the distortion and interaction terms δ_J, h_J, h_{JK}, and f_v. For the ground torsional state, the data included in the fit link adjacent K ladders from $K = 0$ out to $K = 7$ in the A species and between $K = -5$ and $K = +6$ in the E species. In the first excited torsional state only five Q branches are constrained by the data. Other torsionally excited Q branches (and their associated P and R branch b-type transitions) occur at very high (infrared) frequencies and are not directly relevant to the millimeter-wave spectrum.

The spectroscopic constants of Table 1 allow predictions of frequencies for a large number of transitions not yet measured in the laboratory. Predictions for transitions with $J \le 25$, $v_t \le 2$, and $v \le 1500$ GHz may be obtained from one of the authors (E.S.).

e) Fits to $^{13}CH_3OH$ *Data*

For the $^{13}CH_3OH$ isotopic species Anderson, Herbst, and De Lucia (1987) provide a compilation of 364 lines with $J \le 9$ and $v_t \le 2$. To this we have added 91 lines with $v < 100$ GHz out to $J = 22$ and with $v_t \le 2$ from the laboratory study of Kuriyama *et al.* (1986). The quality of the fit is good even out to this high a J value. The $^{13}CH_3OH$ data set is rather less extensive than that for $^{12}CH_3OH$. As a result the data may be fitted with somewhat fewer free parameters in the Hamiltonian. Since the isotopic ratio $^{12}C/^{13}C \sim 30$ (Blake *et al.* 1984) transitions of $^{13}CH_3OH$ detectable in the interstellar medium do not extend to as high energies as for $^{12}CH_3OH$. For example, no torsionally excited lines of $^{13}CH_3OH$ have yet been seen astronomically, although some such transitions might be detectable with somewhat more sensitive receivers. In the ground torsional state observable interstellar lines are currently limited to $J < 16$. The present data set well constrains this ground state between $K = 0$ and $K = 6$ in the A species and between $K = -5$ and $K = +6$ for the E species. The $^{13}CH_3OH$ laboratory data are fitted with 23 adjustable parameters to an overall rms deviation of 2.28 MHz. The derived constants are shown in Table 2 alongside the values given by Anderson, Herbst, and De Lucia (1987). As with

TABLE 2

SPECTROSCOPIC CONSTANTS FOR $^{13}CH_3OH$

Constant (MHz unless noted)	Current Value	Anderson *et al.* 1987
A	127633.91(13)	127633.2572(1231)
B	24077.8(6)	24076.6984(3301)
C	23201.8(6)	23203.5216(3430)
D_{ab}	−88.0(4)	−86.758968(274422)
F (cm^{-1})	27.62938(11)	27.62730724(2400)
ρ (dimensionless)	0.80970381(29)	0.8097058295(2323)
V_3 (cm^{-1})	373.2847(24)	373.2393442(53417)
F_v	−69.25(6)	−69.626967(46463)
G_v	−3.414(6)	−3.404674(4567)
L_v	−0.035(5)	−0.1036571(68306)
D_{JK}	0.2805(10)	0.2779206(6443)
D_J	0.04691(11)	0.04815791(17263)
D_K	1.239(11)	1.0502751(18898)
k_1	−3.8 (fixed)	−3.8 (fixed)
k_2	−80.0 (fixed)	−80.0 (fixed)
k_3	−132.0 (fixed)	−132.0 (fixed)
k_4	−249.0 (fixed)	−249.0 (fixed)
k_5	161.0 (fixed)	161.0 (fixed)
k_6	884.0 (fixed)	884.0 (fixed)
k_7	0.0 (fixed)	0.0 (fixed)
δ_J	0.00222(17)	0.0 (fixed)
δ_K	−0.038(20)	−0.0908806(508230)
c_1	−1.09(9)	−1.128900(33873)
c_2	3.0(9)	4.60584(51350)
V_6 (cm^{-1})	−0.80 (fixed)	−0.80 (fixed)
H_J	0.0 (fixed)	0.0 (fixed)
H_{JK}	0.000011(6)	0.0 (fixed)
H_{KJ}	0.0 (fixed)	0.0 (fixed)
H_K	−0.00169(27)	−0.01058944(77888)
h_J	0.0000006(5)	0.0 (fixed)
h_{JK}	0.00054(4)	0.0 (fixed)
h_K	−0.0178(7)	0.0 (fixed)
f_v	0.0 (fixed)	0.0 (fixed)
c_3	−0.014(4)	0.0 (fixed)

NOTES.—Figures in parentheses represent 1 σ uncertainties in the least significant digits.

$^{12}CH_3OH$, frequency predictions out to $J = 25$ based on these constants may be obtained from the authors.

III. DISCUSSION

a) Normal ($^{12}CH_3OH$) *Methanol*

A variety of methanol lines have been observed astronomically, beginning with the work of Ball *et al.* (1970). Lovas *et al.* (1982) observed the first torsionally excited lines of methanol, indicating that interstellar methanol was often excited up to rather high energy levels. In assigning interstellar lines the *a*-type spectrum of methanol has been fairly well understood, in part due to the fact that only relatively low J levels are involved in microwave and millimeter wave *a*-type lines. The *b*-type spectrum has been less well understood except in special cases where there are low-frequency Q-branches which have been well studied in the laboratory. The existence of high excitation regions of interstellar methanol means that for *b*-type transitions it will be necessary to consider simultaneously high values of both J ($J \sim 22$) and K ($K \sim 7$). Interstellar methanol lines have been observed from levels with excitation energies of up to 600 cm^{-1}, measured from the bottom of the torsional potential barrier.

The interstellar transitions of $^{12}CH_3OH$ which we have been able to assign are listed in Table 3. The majority of these are *b*-type R-branch transitions in the ground torsional state. For most of these the assignment is unambiguous. As an example, the line at 227814.5 MHz is assigned to the transition 16_1–15_2 $A+$. The frequency predicted by our calculations is 227814.6 with a formal error of 2.1 MHz. This transition is well determined since laboratory frequencies exist for numerous other members of this *b*-type series, ranging from 3_2–4_1 $A+$ out to 14_1–13_2 $A+$. Most of the transitions in Table 3 are similarly well determined: they are closely related to numerous assigned transitions which have been measured to high precision in the laboratory and they have been checked by error curve analysis.

The $K = 1$–0 E species Q branch is somewhat more troublesome. The low J members of this Q branch occur at frequencies around 165 GHz, but at higher J these lines shift toward higher frequency. The lines become sufficiently widely spaced that the band structure is no longer very obvious. Laboratory frequencies for this band were obtained by Lees and Baker (1968) out to $J = 17$. In Table 3 we report assignments for the $J = 20$, 21, and 22 members of this series. These represent a substantial extrapolation from the laboratory data set and the formal uncertainties in the predicted frequencies (~5–10 MHz) are considerably larger than for the other assignments. Due to potential inadequacies in the Hamiltonian, these formal uncertainties may be regarded as lower limits to the actual uncertainties. Despite the relatively large errors in the predicted absolute frequencies we feel fairly confident in these assignments due to the regular spacing of these lines, which is very nearly that expected. We cannot find any alternate methanol transitions capable of explaining the lines assigned here to the $J = 20$, 21, and 22 members of this Q branch. As will be discussed below, the strengths of the observed astronomical lines are also consistent with these identifications. The complete error curve for this Q branch is shown in Figure 1. In this graph the difference between observed and predicted frequencies is plotted versus J. The validity of the identifications of the three high J lines is clear, even though the magnitude of the frequency difference becomes quite large. This behavior is fairly typical for our analysis. For most of the data the quality of the frequency predictions is quite good below $J = 20$ but begins to deteriorate markedly somewhere between $J = 20$ and $J = 25$.

The most problematic assignment concerns the line at 247840.2 MHz. Based simply on a predicted frequency of 247886.5 ± 6.8 MHz, one possible assignment would be the 23_1–23_0 E Q-branch line of the ground torsional state. However this can be ruled out based on error curve analysis. The most likely assignment seems to be the 12_{-2}–13_{-3} E

TABLE 3

TRANSITIONS OF $^{12}CH_3OH$

Frequency (MHz)	Residual[a] (MHz)	v_t	J_K	E_{upper} (cm^{-1})	T_a^* (K)	$\int T_a^* dv$ (K km s^{-1})	Astronomical Reference[b]	Laboratory Reference[b]
211804.	−3.	1	16_2–15_1 $A-$	554.1	0.6	3.5	Sut85[c]	...
213159.21	−4.0	0	20_{-4}–19_{-5} E	527.3	0.5	1.7	Sut85[c]	Sas84
213379.	−15.	0	13_6–14_5 E	398.7	0.6	4.0	Sut85[c]	...
213428.	2.	0	1_1–0_0 E	143.9	5.4	22.5	Sut85[c]	...
217299.202	3.5	1	6_1–7_2 $A-$	387.7	1.2	8.3	Sut85	Her84
217886.6	8.3	0	20_1–20_0 E	481.0	0.9	6.7	Sut85	Sut85[d]
222722.9	−8.2	1	16_2–15_1 $A+$	554.1	0.6	2.1	Sut85	Sut85[d]
224699.4	22.2	0	20_{-2}–19_{-3} E	485.1	0.7	3.7	Sut85	Sut85[d]
227094.6	19.3	0	21_1–21_0 E	514.9	0.9	4.8	Sut85	Sut85[d]
227814.5	−0.1	0	16_1–15_2 $A+$	355.1	1.4	6.9	Sut85	Sut85[d]
229589.1	−10.7	0	15_4–16_3 E	387.9	1.3	7.1	Sut85	Sut85[d]
232945.	−7.	0	10_{-3}–11_{-2} E	260.0	3.0	20.0	Sut85	...
237129.4	37.0	0	22_1–22_0 E	550.3	0.7	4.5	Sut85	Sut85[d]
239731.4	−25.3	0	16_7–17_6 $A\pm$	517.0	0.6	1.7	Sut85	Sut85[d]
247162.1	13.4	0	16_2–15_3 E	362.7	1.6	17.4	Bla86	Bla86[d]
247840.2[e]	32.5	1	12_{-2}–13_{-3} E	506.7	1.0	4.9	Bla86	Bla86[d]
259273.7	−2.6	1	17_2–16_1 $A-$	581.4	1.0	5.0	Bla86	Bla86[d]
281958.	−5.	0	9_{-3}–10_{-2} E	243.9	...	...	Lor81	...

[a] $\nu_{observed} - \nu_{calculated}$; an error curve diagram showing the largest of these residuals is given in Figure 1.

[b] See list of references for abbreviations.

[c] This transition was observed at the same time as the data of Sutton *et al.* (1985), but was outside of the published frequency range.

[d] Laboratory frequency measurements by Blake and Pickett (unpublished) as reported in Sutton *et al.* (1985) and Blake *et al.* (1986).

[e] Tentative assignment.

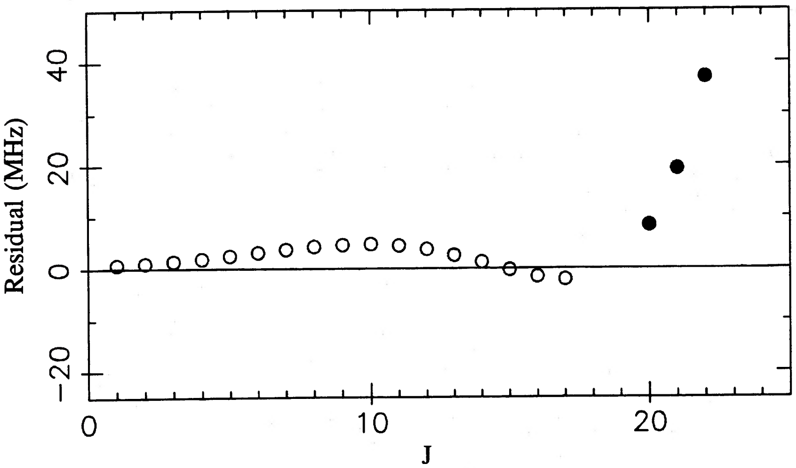

FIG. 1.—Error curve analysis of the $v_t = 0$ $K = 1$–0 E species Q branch. The frequency difference $\nu_{\rm observed} - \nu_{\rm calculated}$ is plotted vs. the rotational quantum number J. Open symbols illustrate the fit to the $J = 1$–17 data of Lees and Baker (1968) and Sastry *et al.* (1984). Filled symbols refer to the assignments at $J = 20, 21$, and 22 discussed here. The residual at $J = 22$ is quite large, but the identifications are clearly correct.

b-type transition in the first excited torsional state, for which the predicted frequency is 247807.7 ± 6.5 MHz. Unfortunately this assignment cannot be checked by error curve techniques since none of the related *b*-type lines (linking the $K = -2$ and $K = -3$ $v_t = 1$ E ladders) have been measured in the laboratory. Although there do not appear to be any other alternatives, this assignment should be viewed as tentative, pending additional laboratory measurements. As discussed below, the strength of the astronomical emission is consistent with that expected for this torsionally excited line.

A completely different approach to frequency predictions for methanol can be based on the work of the Italian group (Moruzzi *et al.* 1986; Carnesecchi, Moruzzi, and Strumia 1987). These authors fit the far-infrared spectrum of methanol using empirical Taylor series representations for the energy levels, an approach employed earlier by Pickett *et al.* (1981). Carnesecchi *et al.* are able to describe the fits to over 12,000 far-infrared lines using a total of 428 adjustable Taylor series coefficients. Generally these series are very good at predicting the frequencies of the microwave and millimeter-wave transitions, allowing for the somewhat lower resolution of the far-infrared data. But in some cases this is not true. For example, the frequency predicted for the transition 14_1–13_2 $A+$ differs from that measured by Lees and Baker (1968) by over 1 GHz. In comparing the Taylor series predictions with the results in Table 3 there is good agreement with the present work for the majority of the newly assigned lines. Significant discrepancies occur however for several assignments, particularly those involving large vaues of J, illustrating the limitations in extrapolating such power-law relations beyond the data originally fit.

b) Isotopic ($^{13}CH_3OH$) *Methanol*

A modest number of $^{13}CH_3OH$ lines have been detected in the interstellar medium in the sources Sgr B2 and OMC 1 (see, e.g., Gottlieb *et al.* 1979; Blake *et al.* 1984; Johansson *et al.* 1984). Recently Blake *et al.* (1986) observed a band of lines in OMC 1 around 255 GHz. They were unable to assign these transitions, but from the laboratory spectrum were able to show they were due to emission from methanol. These lines were subsequently measured in the laboratory and assigned to transitions in the $K = 3$–2 A species Q branches of $^{13}CH_3OH$ by Anderson *et al.*, who however did not point out the correspondence with the astronomical observations. We note these assignments in Table 4 along with the existence of five other interstellar lines from these Q branches present in the data set of Blake *et al.* (1986). These were not originally claimed as detections but were evident once the frequencies of the lines in this band were known. Of these five lines, two were measured by Anderson *et al.* The frequencies of the remaining three were predicted by those authors and confirmed by our calculations.

Other than Q branches such as that described above or *a*-type bands such as that seen by Blake *et al.* (1984), emission from isotopic methanol will be confined to numerous isolated *b*-type transitions ($\Delta J = \pm 1$). Several lines of this sort are also listed in Table 4. In particular we note that a *b*-type line at 163873 MHz measured by Anderson *et al.* corresponds to a previously unidentified astronomical line reported by Snyder, Schenewerk, and Hollis (1985). Three other P branch *b*-type transitions measured by Anderson *et al.* at 215887, 256672, and 259987 MHz may also be seen in the astronomical data.

c) Strengths of Astronomical Emission

Frequency predictions alone are, at best, a rather risky basis for transitional assignments. Spectroscopists often use some additional procedure (e.g., Stark effect spectroscopy) to confirm the identifications. In this case we use the intensities of the astronomical detections as an additional form of identification. It is convenient to plot the astronomical intensities using what is known as the rotation diagram technique. In this method the integrated intensity, stated in the form

$$\frac{3k}{8\pi^3 \nu \mu^2 S} \int T_b \, dv \,,$$

is plotted against the upper state energy. If the molecular cloud is optically thin and in thermal equilibrium the observed data will form a straight line whose slope yields the cloud temperature and whose intercept, after multiplication by a rotational partition function, gives the molecular column density. We have applied this method to those lines in Tables 3 and 4 derived from the measurements of Sutton *et al.* (1985) and Blake *et al.* (1986), data sets with identical calibration. The astronomical intensities used, some previously unreported, are

TABLE 4

TRANSITIONS OF $^{13}CH_3OH$

Frequency (MHz)	Residual[a] (MHz)	v_t	J_K	E_{upper} (cm^{-1})	T_a^* (K)	$\int T_a^* dv$ (K km s^{-1})	Astronomical Reference[b]	Laboratory Reference[b]
163872.900	−0.6	0	$7_0–6_1$ E	181.0	...	...	Sny85	And87
215886.963	0.4	0	$4_2–3_1$ E	159.1	0.9	3.3	Sut85	And87
254841.818	1.6	0	$8_3–8_2$ A− −A+	219.3	0.7	2.0	Bla86[c]	And87
254959.398	1.0	0	$7_3–7_2$ A− −A+	206.7	1.2	5.5	Bla86	And87
255050.965	0.3	0	$6_3–6_2$ A− −A+	195.7	...	...	Bla86[d]	And87
255120.837	−0.3	0	$5_3–5_2$ A− −A+	186.3	1.7	3.2	Bla86	And87
255173.019	−0.7	0	$4_3–4_2$ A− −A+	178.4	1.2	4.0	Bla86	And87
255193.329	0.7	0	$5_3–5_2$ A+ −A−	186.3	1.8	8.1	Bla86	And87
	0.0	0	$6_3–6_2$ A+ −A−	195.7			Bla86	And87
255203.728	−0.7	0	$4_3–4_2$ A+ −A−	178.4	1.3	2.8	Bla86	And87
255210.605	−1.1	0	$3_3–3_2$ A− −A+	172.1	0.6	1.5	Bla86[c]	And87
255214.891	0.6	0	$7_3–7_2$ A+ −A−	206.7	1.0	2.8	Bla86	And87
255220.865	−1.1	0	$3_3–3_2$ A+ −A−	172.1	0.9	2.7	Bla86	And87
255265.637	1.1	0	$8_3–8_2$ A+ −A−	219.3	1.4	5.2	Bla86	And87
255357.	2.	0	$9_3–9_2$ A+ −A−	233.5	1.0	3.5	Bla86[c,e]	...
255498.	2.	0	$10_3–10_2$ A+ −A−	249.2	0.8	2.6	Bla86[c,e]	...
255980.	−1.	0	$12_3–12_2$ A+ −A−	285.4	0.5	2.9	Bla86[c,e]	...
256671.817	−1.4	0	$9_0–8_1$ E	207.7	0.5	4.5	Bla86[c]	And87
259986.530	0.7	0	$2_1–1_0$ E	147.2	...	...	Bla86[f]	And87

[a] $\nu_{observed} - \nu_{calculated}$.

[b] See list of references for abbreviations.

[c] Not listed as detected lines by Blake *et al.* (1986) but evident in the data.

[d] Blended with the $5_{2,3}–4_{3,2}$ line of HDO.

[e] Frequency predictions by Anderson *et al.* (1987) and this work.

[f] Listed as unidentified line, too broad and strong to be entirely due to methanol.

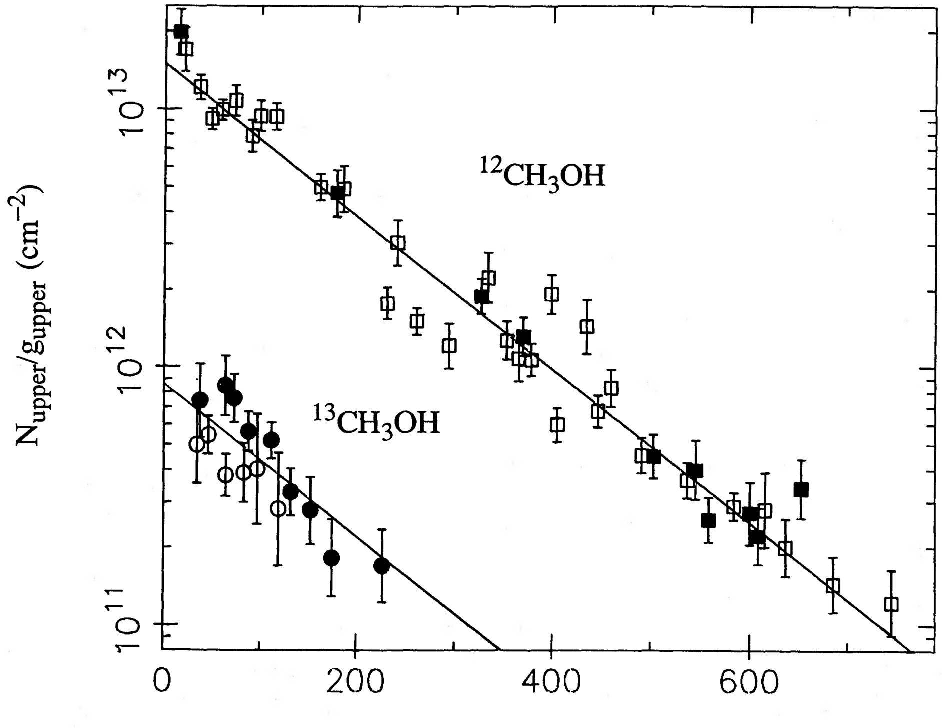

FIG. 2.—Rotation diagram analysis of methanol emission from OMC 1. Filled symbols designate transitions newly assigned in this work, contrary to the previous usage in Blake *et al.* (1987) where they denoted torsionally excited lines. No special designation is made here for lines from the first torsionally excited state. Some data points in this figure have been combined to avoid crowding. Upper state energies shown are measured with respect to the lowest lying level of each symmetry species. For $^{12}CH_3OH$ these zero-point energies are 127.7 cm^{-1} (*A*) and 133.2 cm^{-1} (*E*) and for $^{13}CH_3OH$ are 127.9 cm^{-1} (*A*) and 133.3 cm^{-1} (*E*) above the bottom of the torsional potential barrier.

included in Tables 3 and 4. In Figure 2 these data are plotted alongside the previously determined rotational data for methanol from Blake *et al.* (1987). The newly identified lines are indistinguishable, in terms of inferred column densities, from the previous data set. The combined data yield a rotational temperature of $T = 146.2 \pm 2.7$ K and $N_c = 3.26 \pm 0.14 \times 10^{16}$ cm^{-2} for $^{12}CH_3OH$ and $T = 146.6 \pm 30$ K and $N_c = 1.88 \pm 0.27 \times 10^{15}$ cm^{-2} for $^{13}CH_3OH$.

IV. SUMMARY

Through application of modern supercomputing techniques we have extended the use of the internal axis method (IAM) analysis of the spectrum of methanol out to large quantum numbers. Laboratory data for 783 lines of $^{12}CH_3OH$ from the lowest three torsional levels out to a rotational quantum number of $J = 22$ are fitted to an rms deviation of 4.40 MHz. Similarly for $^{13}CH_3OH$ 455 lines out to $J = 22$ are fitted to an rms of 2.28 MHz. These represent considerable extensions over the previous IAM limits of $J = 8$ for $^{12}CH_3OH$ (Herbst *et al.* 1984) and $J = 9$ for $^{13}CH_3OH$ (Anderson, Herbst, and De Lucia 1987).

This analysis has permitted the identification of a number of previously unassigned interstellar methanol lines. A total of 16 lines of $^{12}CH_3OH$ are newly identified. All of these lines are from the 250 GHz region, a part of the spectrum which has not been extensively studied in the laboratory. All of these lines are *b*-type; to date the *b*-type spectrum has been the most difficult to analyze. For $^{13}CH_3OH$ the assignments of 18 interstellar lines are discussed. Six of these lines were not previously reported in the astronomical literature. For both the $^{12}CH_3OH$ and $^{13}CH_3OH$ lines the astronomical intensities seen toward OMC-1 are shown to be consistent with rotational temperatures of 146.2 ± 2.7 K (^{12}C) and 146.6 ± 30 K (^{13}C) and column densities of 3.26 ± 0.14 10^{16} cm^{-2} (^{12}C) and 1.88 ± 0.27 10^{15} cm^{-2} (^{13}C).

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