

MICROWAVE SPECTRUM OF ^{13}C METHANOL

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ABSTRACT

Laboratory measurements of the frequencies of some astronomically interesting transitions of the ^{13}C isotopic species of methanol are reported. Most lines of the $J = 2 \leftarrow 1, 3 \leftarrow 2, 4 \leftarrow 3$ μ_a -type $\Delta k = 0$ transitions in the 94-, 142-, and 189-GHz regions have been measured, as well as a number of μ_b -type transitions in the 14–50 GHz region. The standard deviation of fit with the constants given is 0.098 MHz. The remaining unmeasured lines in these R -branch patterns have been predicted with an uncertainty of 0.3 MHz.

Subject headings: line identifications — molecules, interstellar

Methanol is becoming one of the more interesting and important interstellar molecules, as at present more rotational lines have been observed astronomically for it than for any other molecule, and these lines tend to occur in close groups encompassing a wide range of quantum numbers and excitation energies. Thus, methanol is a particularly good probe of the physical conditions of the dense interstellar clouds in which it is observed. There is presently some uncertainty as to the conditions of excitation of the methanol in these clouds, as the observation of the $J_k = 5_{-1} \rightarrow 4_0$ (E) and $4_{-1} \rightarrow 3_0$ (E) lines in Sgr B2 coupled with their absence in Ori A suggested an anomalous nonequilibrium excitation (Zuckerman *et al.* 1972; Turner, Gordon, and Wrixon 1972), whereas the relative intensities of the members of the $k = 2 \rightarrow 1$ (E) Q -branch in Ori A (Barrett, Schwartz, and Waters 1971) and the recently detected lines of the $J = 3 \rightarrow 2$ $\Delta k = 0$ μ_a -type transition in Ori A (Kutner *et al.* 1973) appear quite consistent with LTE excitation. (The notation used here for labeling transitions is that proposed recently by Lees 1973. Lines of the E species with positive k -values have previously been called E_1 , and those with negative k -values have been called E_2 .) It appears that astronomical detection of analogous lines of the ^{13}C isotopic species of methanol would provide very useful additional information for the determination of excitation conditions, optical depths, and number densities. As relatively few ^{13}C methanol rotational lines have been measured to date (Lees *et al.* 1973), we have conducted a more extensive study, and report here frequencies of the important μ_a -type transitions in the millimeter wave region, and those of a number of μ_b -type transitions in the conventional microwave region.

The frequencies below 50 GHz were measured at the University of New Brunswick on a standard 85-kHz Stark-modulated spectrometer with an X -band absorption cell, those around 94 GHz at the National Bureau of Standards in Washington on a millimeter-wave parallel-plate Stark spectrometer, and those above 140 GHz at the National Bureau of Standards in Boulder on a second millimeter-wave Stark spectrometer, the operation and characteristics of which have been previously described (Beers and Klein 1972).

The μ_a -type lines were assigned on the basis both of their Stark effects and agreement with predictions made from a Kirtman first-order perturbation formula (Kirtman 1962; Lees and Baker 1968). The frequencies are listed in table 1, together with their estimated measurement accuracies and the deviations from the frequencies calculated by a least-squares fit to the Kirtman formula. For completeness, and to show the quality of the least-squares fit, all of the frequencies used in the fit are listed in table 1, including those of the $J = 1 \leftarrow 0$ transition previously reported by Venkateswarlu, Edwards, and Gordy (1955). In the least-squares analysis, all frequencies were equally weighted, and were fitted with a standard deviation of 0.098 MHz.

As not all of the lines of the $2 \leftarrow 1$ and $4 \leftarrow 3$ transitions were measured experimentally, the calculated frequencies of the unmeasured lines are presented in table 1, enclosed in asterisks, and should be accurate to ± 0.3 MHz. For reference, the molecular constants used in the calculations are given in table 2. The values are the ones obtained in the least-squares fit, and are presented along with their least-squares rms errors. The values found for $\frac{1}{2}(B + C)_V$, F_V , and G_V are similar to those derived previously by Nishikawa (1956), while

TABLE 1
 $^{13}\text{CH}_3\text{OH}$ μ_a -TYPE FREQUENCIES (in MHz)*

TRANSITION			A LINES†			E LINES		
$J \leftarrow J'$	k	v	ν	Est. Acc. (MHz)	$\nu_{\text{obs}} - \nu_{\text{calc}}$	ν	Est. Acc. (MHz)	$\nu_{\text{obs}} - \nu_{\text{calc}}$
1 ← 0	0	0	47,205.20†	(0.5)	0.008	47,209.63‡	(0.5)	-0.002
	0	1	47,094.11‡	(0.5)	0.088	47,083.82‡	(0.5)	-0.089
	0	2	47,030.16‡	(0.5)	-0.008	** 47,017.2**	(0.5)	...
2 ← 1	0	0	94,407.02	(0.1)	-0.092	94,410.76	(0.1)	-0.151
	1	0	**93,619.5**	(0.3)	...	94,420.36	(0.15)	+0.016
	-1	0	**95,208.7**	(0.3)	...	94,405.17	(0.15)	+0.034
3 ← 2	0	0	141,602.528	(0.04)	0.042	141,595.477	(0.05)	-0.006
	1	0	140,423.830	(0.04)	-0.023	141,629.262	(0.025)	+0.044
	-1	0	142,807.657	(0.04)	-0.023	141,597.059	(0.05)	+0.049
	2	0	141,630.908	(0.04)	-0.005	141,623.491§	(0.025)	-0.047
	-2	0	141,622.715	(0.04)	-0.005	141,623.491§	(0.025)	+0.156
4 ← 3	0	0	188,788.029	(0.05)	-0.015	188,754.921	(0.05)	-0.075
	1	0	**187,221.8**	(0.3)	...	188,836.430	(0.05)	-0.106
	-1	0	**190,400.2**	(0.3)	...	188,776.224	(0.05)	+0.173
	2	0	**188,840.5**	(0.3)	...	**188,839.9**	(0.3)	...
	-2	0	188,820.021§	(0.05)	-0.037	**188,839.1**	(0.3)	...
	3	0	**188,802.2**	(0.3)	...	188,804.920	(0.05)	-0.113
	-3	0	**188,802.3**	(0.3)	...	188,820.021§	(0.05)	+0.059

* Frequencies enclosed in asterisks are calculated. All others are observed.

† The A^+ and A^- components of a k -doublet are listed under $+k$ and $-k$, respectively. Only the average of the A^+ and A^- frequencies, i.e., the doublet center, was used in the least-squares fit, hence the $(\nu_{\text{obs}} - \nu_{\text{calc}})$ quoted for a doublet is that of the average frequency.

‡ Measured by Venkateswarlu *et al.* (1955).

§ Not resolved.

TABLE 2

^{13}C H_3OH MOLECULAR PARAMETERS USED IN CALCULATION
 OF μ_a -TYPE FREQUENCIES

Parameter*	(RMS Error)†
$\frac{1}{2}(B+C)_v$	23,640.058 (22) MHz
F_v	-69.583 (47) MHz
G_v	-3.3916 (61) MHz
L_v	-0.022 (22) MHz
D_{JK}	0.2827 (23) MHz
D_J	0.04812 (57) MHz
D_{ab}	-84.96 (98) MHz
$(B-C)_v$	864.18 (83) MHz
α	3.38316
ρ	0.81059

* Parameters are defined by Lees and Baker (1968).

† Values may be refined slightly in future, as further work is in progress. They should be regarded as preliminary. The numbers in parentheses represent the error in the last two significant figures and should be interpreted as one standard deviation from the stated value.

L_v turns out to be essentially undetermined by the present data. In the calculation of the torsional matrix elements for use in the Kirtman formula, the reduced parameters α and ρ , defined in the Appendix of Lees and Baker (1968) are required. The values of α and ρ given in table 2 are preliminary, as they were obtained from fitting a few rather poorly determined Q -branch origins

to just the axial moments of inertia I_{a1} and I_{a2} and the barrier height V_3 . This work is being extended and refined, and will be presented elsewhere. As revision of α and ρ in future will modify the μ_a -type parameters of table 2 to some extent, these should also be regarded as preliminary, but they are not very sensitive to α and ρ so the calculated frequencies should not change by more than the estimated ± 0.3 MHz.

Finally, additional measurements were made of a number of μ_b -type transitions in the conventional 8-50 GHz microwave region. The frequencies and assignments are presented in table 3. The list includes the

TABLE 3

$^{13}\text{CH}_3\text{OH}$ μ_b -TYPE FREQUENCIES (in MHz)*

Transition	ν_{obs}	Transition	ν_{obs}
$5_1 \leftarrow 6_0 (A^+)$	14,300.63	$2_1 \leftarrow 3_0 (E)$	23,980.18
$7_0 \leftarrow 6_1 (A^+)$	35,161.58	$4_0 \leftarrow 3_1 (E)$	23,145.40
$4_2 \leftarrow 5_2 (A^+)$	19,123.48	$2_0 \leftarrow 3_{-1} (E)$...	14,782.15
$4_2 \leftarrow 5_2 (A^-)$	19,195.44	$4_{-1} \leftarrow 3_0 (E)$	32,398.45†
$6_2 \leftarrow 5_3 (A^+)$	28,137.37	$7_{-2} \leftarrow 8_{-1} (E)$...	48,529.52‡
$6_2 \leftarrow 5_3 (A^-)$	27,992.53	$10_{-1} \leftarrow 9_{-2} (E)$...	44,294.37

* Estimated accuracy is ± 0.1 MHz. All transitions are for the torsional ground state, $v = 0$.

† Reported but not assigned by Hughes *et al.* (1951).

‡ Reported but not assigned by Venkateswarlu *et al.* (1955).

important $4_{-1} \leftarrow 3_0$ (E) transition detected in Sgr B2 for normal methanol (Turner *et al.* 1972) but not, unfortunately, the equally significant $5_{-1} \leftarrow 4_0$ (E) transition (Zuckerman *et al.* 1972). However, being able to calculate quite accurate μ_a -type frequencies, we can calculate the differences between successive members of a μ_b -type series equally accurately; hence by

extrapolating from the observed $4_{-1} \leftarrow 3_0$ (E) frequency, we predict a frequency of $79,581.3 \pm 0.5$ MHz for the $5_{-1} \leftarrow 4_0$ (E) line.

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