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Microwave and Submillimeter-Wave Spectra of CH_3OH

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Frequency measurements and assignments have been made for CH_3OH lines in the 15- to 400-GHz region. The *a*-type *R*-branch multiplets are reported up to $J = 8 \leftarrow 7$ for the $v_t = 0$ torsional ground state, and to $J = 6 \leftarrow 5$ for the $v_t = 1$ and $v_t = 2$ excited states. Several new *Q* branches are listed and many *b*-type *P*- and *R*-branch transitions have been identified over a wide range of *J* and *k* values.

1. INTRODUCTION

Over the past 3 decades, numerous studies of various portions of the microwave and millimeter-wave spectra of CH_3OH from 8 to 200 GHz have been carried out, and a good understanding of the energy level structure in the ground torsion–vibration state has been achieved up to moderate values of the rotational quantum numbers (*1–12*). Recently, the spectrum was examined up to 850 GHz by Pickett *et al.* (*13*), and many transitions in the 200- to 850-GHz region were reported. Extension of knowledge of the spectrum to this higher frequency submillimeter region is important not only to permit improvement of the model for the Hamiltonian and the molecular parameters, but also in connection with current developments in molecular radio astronomy and optically pumped far-infrared (FIR) lasers.

In radio astronomy, with progress in telescope dish figuring and receiver technology, millimeter telescopes are beginning to operate routinely above 200 GHz. In this frequency range, transitions of the more abundant and well-known of the molecules found as constituents of large interstellar clouds can be extremely strong, standing out like "searchlights" in the emission spectra from the clouds. Thus, even relatively weak or highly excited transitions of these molecules may still be detectable, and could mask the emission from new and interesting species in the clouds. Methyl alcohol has acquired some notoriety in this respect, through its wide variety of lines scattered across the entire microwave, millimeter, and submillimeter bands. Furthermore, in a rich interstellar source such as Orion A, CH_3OH emission can be detected from rotational and torsional levels up to rather high excitation energies of about 350 cm^{-1} above the ground state (*14, 15*). Thus, while methanol lines do offer a good data base for excitation studies and temperature probes, they tend nowadays

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to be regarded rather more as "weeds" in the astronomical garden, and a more extensive catalog of CH_3OH lines is desirable to allow molecular astronomers to pick them out.

In the area of FIR lasers, on the other hand, the density and diversity of the methanol infrared spectrum around 10 μm are of great advantage. CH_3OH can be optically pumped in the C—O stretch vibrational band by numerous CO_2 laser lines to yield a large group of FIR lasing transitions. Henningsen (*16*) has recently reviewed the current state of understanding of the methanol FIR laser emission and of the extensive diode laser spectra of the C—O stretch region reported by Sattler *et al.* (*17*). Many of the FIR laser and infrared pump lines appear to involve levels of high J and k rotational quantum number and levels in excited torsional states, for which energy calculations in neither the ground nor excited vibrational state are yet sufficiently precise to lead to confident assignments. Therefore, measurements of rotational transitions of high J and k or with torsional quantum number $v_t > 0$ are useful for the construction of a more complete and accurate ground state energy level picture. This should serve to establish reliable combination difference loops for identification of additional lines in the infrared spectrum, and should thereby lead to further assignments of FIR laser and infrared pump transitions.

The present study was carried out to increase the range of CH_3OH spectroscopic data available for application in radio astronomical and FIR laser line identification and for future development and testing of better models for the methanol Hamiltonian and molecular parameters. In this paper, we report frequency measurements and assignments for several hundred CH_3OH transitions over the 15- to 400-GHz region.

2. EXPERIMENTAL ASPECTS

All line frequencies above 200 GHz were measured at Duke University employing the submillimetric techniques described previously (*18*). Submillimeter power was derived from a harmonic multiplier driven by a 50-GHz fundamental klystron, optically focused through a free-space absorption cell, and detected by a helium-cooled InSb bolometer.

The lines below 105 GHz were observed at the University of New Brunswick on a standard Stark-modulated spectrometer as described previously (*19*), employing a 6-ft K-band absorption cell and phase-locked klystron sources. Frequency measurements were made with a Hewlett–Packard 5340A frequency counter, referenced to an EFROTOM 5-MHz rubidium frequency standard.

All measurements were made at room temperature, with pressures varying from 10 to 100 mTorr as appropriate to optimize frequency accuracy. In general, the accuracy for new lines below 105 GHz is estimated to be ±0.1 MHz. Above 200 GHz, with the absence of Stark broadening, a better accuracy of ±0.05 MHz is estimated, with measurements referenced to the WWVB standard broadcast.

3. RESULTS

The observed frequencies have been separated into three classes, which are listed in Tables I to III, respectively. Table I includes the components with different k and

TABLE I

Observed CH_3OH *a*-Type *R*-Branch Frequencies (in MHz)

Transition			E Lines[a,b]				A Lines[a,c]		
$J' \leftarrow J''$	v_t	k	$\nu_o(+k)$	$\nu_o-\nu_c$[d]	$\nu_o(-k)$	$\nu_o-\nu_c$[d]	$\nu_o(A+)$	$\nu_o(A-)$	$\nu_o-\nu_c$[d]
5 ← 4	0	0	241 700.10[e]	0.62	-	-	241 791.39[e]	-	0.10
		1	241 879.05[e]	-0.67	241 767.25[e]	0.61	239 746.21[e]	243 915.76[e]	-0.47
		2	241 904.39[e,f]	-2.07	241 904.39[e,f]	-0.37	241 887.65[e]	241 842.26[e]	-0.71
		3	241 843.70[e]	-1.07	241 852.31[e]	-0.82	241 832.91[e]		0.37
		4	241 829.61[e]	-1.19	241 813.27[e]	1.26	241 806.51[e]		-1.51
	1	0	241 205.99	0.32	-	-	241 267.88	-	-1.89
		1	241 203.69	0.13	241 238.16	-0.57	240 960.56	241 441.24	0.35
		2	241 210.68	-3.33	241 187.40	-0.02	241 192.81	241 196.35	-0.23
		3	241 166.53	3.57	241 179.90	-0.68	241 198.29		-0.17
		4	241 159.13	-1.78	241 184.08	0.86	241 178.42		2.45
	2	0	240 869.49	0.43	-	-	240 938.94	-	0.41
		1	240 817.94	-0.04	240 958.80	-0.54	240 454.85	241 364.12	1.22
		2	240 952.07	-1.14	240 936.73	2.12	240 757.91		-0.13
		3	240 948.33	3.23	240 752.53	8.06	240 916.16		-0.96
		4	240 784.26	10.21	240 861.55	-0.89	240 932.02		3.82
6 ← 5	0	0	289 939.37[e]	1.82	-	-	290 110.64[e]	-	0.02
		1	290 248.71[e]	-1.48	290 069.74[e]	0.91	287 670.78[e]	292 672.89	-0.61
		2	290 307.48[e,f]	-4.23	290 307.48[e,f]	-0.41	290 264.06[e]	290 184.69[e]	-1.14
		3	290 213.20[e]	-1.62	290 209.70[e]	-1.22	290 189.51[e]	290 190.54[e]	-0.01
		4	290 183.21[e]	-1.69	290 162.43[e]	1.21	290 161.14[e]		-2.30
		5	290 138.89[e]	2.08	290 117.77[e]	-2.39	290 145.09[e]		-2.12
	1	0	289 429.12[g]	-0.06	-	-	289 511.11		-2.60
		1	289 427.60	0.20	289 475.61	-0.97	289 134.05	289 710.46	0.50
		2	289 443.93	-3.78	289 402.49	0.13	289 414.03	289 420.24	-0.15
		3	289 355.02	4.11	289 399.59	-0.83	289 429.75[g]		0.36
		4	289 374.82	-1.95	289 416.36	0.92	289 428.19[g]		1.51
		5	289 423.52	3.38	289 415.09[g]	3.13	289 343.21[g]		-5.10
	2	0	289 031.29	0.50	-	-	289 114.82	-	0.50
		1	288 969.29	-0.04	289 138.82	-0.54	288 533.64	289 624.28	1.41
		2	289 130.62	-1.37	289 111.35	2.47	288 897.11		-0.22
		3	289 125.51	3.86	288 890.43	9.63	289 087.37		-1.23
		4	288 928.50	12.17	289 021.59	-1.24	289 106.11		4.59
		5	288 939.77[g]	-1.34	289 040.90[g]	8.14	288 956.42[g]		13.35
7 ← 6	0	0	338 124.53[e]	4.44	-	-	338 408.71[e]	-	-0.01
		1	338 614.96[e]	-2.72	338 344.55[e]	1.42	335 582.03[e]	341 415.68[e]	-0.78
		2	338 721.63[e]	-8.41	338 722.94[e]	0.19	338 639.86[e]	338 512.76[e,f]	-1.81
		3	338 583.21[e]	-2.26	338 559.99[e]	-1.73	338 540.81[e]	338 543.21[e]	-0.60
		4	338 530.28[e]	-2.14	338 504.11[e]	0.86	338 512.76[e,f]		-2.73
		5	338 475.23[e]	2.00	338 456.52[e]	-3.26	338 486.25[e]		-2.83
		6	338 404.62[e]	-3.19	338 430.93[e]	-3.51	338 442.38[e]		2.77
8 ← 7	0	0	386 247.66	9.83	-	-	386 681.92	-	-0.13
		1	386 977.14	-4.54	386 587.27	2.37	383 477.88	390 141.73	-0.91
		2	387 146.56	-17.06	387 153.55	1.08	387 014.80	386 824.4(0.1)	-2.65
		3	386 953.82	-2.99	386 901.95	-2.39	386 885.54	386 890.12	-1.61
		4	386 869.41	-2.85	386 837.70	0.82	386 859.82		-3.78
		5	386 802.3(0.2)	1.74	386 788.66	-4.39	386 820.0(0.1)		-3.56
		6	386 725.11	-4.38	386 756.93	-4.38	386 764.59		2.72
		7	386 681.92	-6.99	386 716.28	2.87	386 663.56		-3.98

[a] Estimated measurement accuracy is ±0.05 MHz, unless otherwise shown in parentheses.

[b] The +k lines on the left and -k lines on the right correspond respectively to the E_1 and E_2 transitions in previous notation of Ref. 9. See Ref. 20.

[c] A+ lines are listed on the left, A- on the right, and unresolved A± doublets in the centre. For k ≠ 0, the value of $\nu_o - \nu_c$ is for the average of A+ and A- frequencies, i.e. for the centre of the A± doublet.

[d] ν_c is the frequency calculated using the constants of Ref. 9.

[e] Transition first reported in Ref. 13. [f] Blended line. [g] Tentative assignment.

TABLE II

Observed CH_3OH *Q*-Branch Frequencies (in MHz)[a]

J	$k = 1^- \leftarrow 0^+$ A, $v_t = 0$	$k = -2 \leftarrow 1$ E, $v_t = 0$	$k = 3^+ \leftarrow 2^-$ A, $v_t = 0$	$k = 3^- \leftarrow 2^+$ A, $v_t = 0$	$k = 9 \leftarrow 8$ A±, $v_t = 1$
1	303 366.89	-	-	-	-
2	304 208.35	-	-	-	-
3	305 473.52	-	251 917.05[b]	251 905.72[b]	-
4	307 165.94	-	251 900.44[b]	251 866.53[b]	-
5	309 290.40	101 126.8(0.3)	251 890.86[b]	251 811.93[b]	-
6	311 852.65[b]	101 185.32	251 895.70[b]	251 738.42[b]	-
7	314 859.55	101 293.34	251 923.68[b]	251 641.78[b]	-
8	318 318.89[b]	101 469.70	251 984.82[b]	251 517.30[b]	-
9	322 239.45	101 737.08	252 090.38[b]	251 359.88[b]	25 322.98[e]
10	326 630.61	102 122.59	252 252.85[b]	251 164.09[b]	26 550.15[e]
11	331 502.37	102 658.04	252 485.68[b]	250 924.40[b]	27 817.50[e]
12	336 685.11	103 381.11	252 803.38[b]	250 635.19[b]	29 113.76[e]
13	342 729.83	104 336.54	253 221.39	250 291.18	30 429.95
14	349 107.02	105 576.35[c,d]	253 755.85	249 887.47	31 757.42[e]
15	-	107 159.79[c]	254 423.58[f]	249 419.92	33 089.91[e]
16	-	109 153.19[c]	255 241.97	248 885.48	34 417.86[e]
17	-	111 626.53[c]	256 228.80	248 282.46	35 738.32[e]
18	-	114 650.99[c]	257 402.19	247 610.96	37 044.68[e]
19	-	-	258 780.38	246 873.34	38 332.27
20	-	-	260 381.56	246 074.65	-

[a] Estimated measurement accuracy is ±0.1 MHz below 200 GHz, and ±0.05 MHz above 200 GHz, unless otherwise shown in parentheses.

[b] Reported first in Ref. 13. [c] Reported but not assigned in Ref. 9.

[d] Detected as U105577 towards the Kleinmann-Low nebula in Orion. See Refs. 22,23.

[e] Reported but not assigned in Ref. 3. [f] Unresolved from $11_5 \leftarrow 12_4$ E v_t=0 line.

torsional symmetry of the *a*-type ^QR-branch multiplets for $J = 5 \leftarrow 4$ up to $J = 8 \leftarrow 7$ in the $v_t = 0$ torsional ground state, and for $J = 5 \leftarrow 4$ and $J = 6 \leftarrow 5$ in the $v_t = 1$ and $v_t = 2$ excited states. A signed k quantum number is used for transitions of the E torsional species, with $+k$ corresponding to the E_1 lines and $-k$ to the E_2 lines of earlier work (*9, 20*). The values of $(\nu_o - \nu_c)$ quoted in Table I do not represent the results of a fitting procedure, but are simply the differences between the observed frequencies and those calculated using the molecular parameter set of Lees and Baker (*1, 9*).

The frequencies of several extensive Q branches newly observed or assigned are set out in Table II. The $k = -2 \leftarrow 1$, E, $v_t = 0$, Q branch is interesting in that it does not follow the symmetric rotor type of selection rule normally found for CH_3OH, but becomes allowed through the mixing of the $k = +1$ and $k = -1E$ levels induced by the molecular asymmetry. The initial low-J lines of this series are very weak, and we have been unable to detect them below $J = 5$.

In Table III, all other types of transition observed or newly assigned are tabulated in ascending order of frequency, with $v_t = 0$ transitions listed in the first part and $v_t = 1$ transitions in the second. The reported lines are generally *b*-type *P*- or *R*- branch transitions, but several of the *a*-type, $k = 1$, *A*-doublet transitions up to $J = 12$ are also listed, as well as the two members of the $k = 1 \leftarrow 0$, E, Q branch near 167 GHz which were missing from an earlier report (*9*). In addition, we have taken the opportunity in Table III to withdraw several erroneous frequencies reported by Lees and Baker (*9*), for which the multiplier harmonic had been incorrectly identified in the harmonic generation technique used. The reported "line" at 92 836.85 MHz,

TABLE III

Observed CH_3OH *b*-Type and *k* = 1 *A*-Doublet Frequencies (in MHz)[a]

ν_{obs}	J'	k'	J"	k"	TS[b]	ν_{obs}	J'	k'	J"	k"	TS[b]	ν_{obs}	J'	k'	J"	k"	TS[b]
v_t = 0 Ground State Transitions																	
15 214.1(0.5)[c]	25	4^-	24	5^-	A-	83 121.05	22	5^-	23	4^-	A-	234 698.45	5	-4	6	-3	E
15 642.43	25	4^+	24	5^+	A+	84 423.81	13	-3	14	-2	E	236 936.13	14	1^-	13	2^-	A-
16 395.74[d]	16	-2	15	-3	E	84 744.17	19	4	18	5	E	240 241.50[o]	5	3	6	2	E
17 910.82[d,e]	21	3	20	4	E	85 567.97	6	-2	7	-1	E	242 446.21	14	-1	13	-2	E
18 161.44	25	-8	26	-7	E	86 615.76	7	2^-	6	3^-	A-	243 397.53	18	6	19	5	A±
19 140.8(0.2)[d,f]	31	-6	30	-7	E	86 903.06	7	2^+	6	3^+	A+	243 980.31	29	5^+	28	6^+	A+
29 889.33[e,f]	29	-7	30	-6	E	88 594.96	15	3^+	14	4^+	A+	243 997.54	29	5^-	28	6^-	A-
30 193.44[g]	27	-7	26	-8	E	88 940.09	15	3^-	14	4^-	A-	247 228.67[o]	4	2^+	5	1^+	A+
31 977.82[e]	19	4	20	3	E	89 505.74	8	-4	9	-3	E	249 192.80	16	-3	15	-4	E
34 236.91[e]	14	-3	15	-2	E	92 836.85[m]	Nonexistent					249 443.36[o]	7	4^-	8	3^-	A-
40 405.37	14	3^+	13	4^+	A+	94 541.81	8	3	9	2	E	249 451.90[o]	7	4^+	8	3^+	A+
40 635.06	14	3^-	13	4^-	A-	94 815.04[n]	19	7	20	6	A±	250 506.98[o]	11	0^+	10	1^+	A+
41 110.04	9	-4	10	-3	E	95 746.65[n]	25	-6	26	-5	E	254 015.34	2	0	1	-1	E
44 069.49[h]	7	0^+	6	1^+	A+	95 904.70[m]	Nonexistent					254 423.58[p]	11	5	12	4	E
45 818.26	10	1^-	10	1^+	A	98 030.75[n]	24	6	23	7	A±	261 061.36	21	-4	20	-5	E
46 557.97	20	7	21	6	A±	98 267.71	30	-5	29	-6	E	261 704.44	12	6	13	5	E
47 278.62	26	-6	27	-5	E	100 584.13	28	0	28	-1	E	261 805.71	2	1	1	0	E
48 407.74[i]	25	5^+	24	6^+	A+	100 638.90	13	2	12	3	E	262 998.96	30	4^-	29	5^-	A-
48 411.65[i]	25	5^-	24	6^-	A-	104 853.06	27	0	27	-1	E	264 743.98	30	4^+	29	5^+	A+
49 028.32[i]	22	6^-	23	5^-	A-	113 973.44[n]	27	4^-	26	5^-	A-	265 289.65	6	1	5	2	E
49 030.05[i]	22	6^+	23	5^+	A+	114 750.70[n]	27	4^+	26	5^+	A+	266 838.13	5	2	4	1	E
49 725.79	29	-5	28	-6	E	134 231.12[n]	12	-3	13	-2	E	267 403.44	9	0	8	1	E
49 867.83[j]	23	6	22	7	A±	143 097.97[n]	18	7	19	6	A±	267 887.30	24	5	23	6	E
51 759.85	12	2	11	3	E	144 070.82[m]	Nonexistent					268 744.05	9	-5	10	-4	E
54 955.84	11	1^-	11	1^+	A	144 195.11[n]	24	-6	25	-5	E	278 304.51	9	-1	8	0	E
55 673.89	12	-3	11	-4	E	144 351.99[m]	Nonexistent					278 672.92	18	5^+	19	4^+	A+
56 012.37	11	4^-	12	3^-	A-	144 865.63[m]	Nonexistent					278 723.25	18	5^-	19	4^-	A-
56 105.25	11	4^+	12	3^+	A+	149 532.59[n]	14	2	13	3	E	278 965.84	23	4	22	5	E
57 032.92	4	1^+	5	0^+	A+	166 898.65	8	1	8	0	E	279 351.91	11	2^-	10	3^-	A-
57 292.96	10	-1	9	-2	E	167 931.13	9	1	9	0	E	280 679.68	19	3^+	18	4^+	A+
58 394.94	3	3^+	4	2^+	A+	168 577.86	4	1	3	2	E	281 000.2(0.2)	11	2^+	10	3^+	A+
58 429.01	3	3^-	4	2^-	A-	180 440.02[n]	16	4	17	3	E	282 062.70	19	3^-	18	4^-	A-
60 531.42	1	0	2	-1	E	183 720.12[n]	11	-3	12	-2	E	283 094.90	4	-4	5	-3	E
60 690.88	15	5	16	4	E	191 404.23[n]	17	7	18	6	A±	285 111.15	3	2^-	4	1^-	A-
62 906.99	12	1^+	11	2^+	A+	192 626.40[n]	23	-6	24	-5	E	287 234.00	15	-1	14	-2	E
64 537.60[k]	26	4^-	25	5^-	A-	194 243.10[n]	26	6	25	7	A±	288 705.65[o]	4	3	5	2	E
64 907.75	12	1^-	12	1^+	A	196 963.02[n]	13	-1	12	-2	E	291 240.65	15	1^-	14	2^-	A-
65 119.07[k]	26	4^+	25	5^+	A+	201 445.59	5	2^+	6	1^+	A+	291 908.17	17	6	18	5	A±
66 525.23	24	-8	25	-7	E	205 791.27	1	1^+	2	0^+	A+	293 048.70	30	5^+	29	6^+	A+
66 948.01	8	2^+	9	1^+	A+	213 159.21	20	-4	19	-5	E	293 072.69	30	5^-	29	6^-	A-
67 542.23	17	-2	16	-3	E	213 200.09	29	4^-	28	5^-	A-	293 463.99	3	2^+	4	1^+	A+
68 032.06	22	3	21	4	E	214 546.49	29	4^+	28	5^+	A+	302 369.9(0.5)	3	0	2	-1	E
68 252.06[f]	32	-6	31	-7	E	216 945.60	5	1	4	2	E	310 193.00	3	1	2	0	E
68 305.63	1	1	2	0	E	218 440.05	4	2	3	1	E	313 596.84	7	1	6	2	E
68 554.70	16	6	17	5	E	229 758.76	8	-1	7	0	E	315 266.83	6	2	5	1	E
69 055.01	17	-4	16	-5	E	229 864.19	19	5^+	20	4^+	A+	350 687.73	4	0	3	-1	E
75 515.35	13	-5	14	-4	E	229 939.18	19	5^-	20	4^-	A-	350 905.07[o]	1	1^+	0	0^+	A+
75 943.58	20	5	19	6	E	230 027.06	3	-2	4	-1	E	358 605.80	4	1	3	0	E
76 247.27[ℓ]	11	1^-	10	2^-	A-	230 368.69	22	4	21	5	E	363 739.82	7	2	6	1	E
76 509.67[ℓ]	5	0	4	1	E	231 281.10	10	2^-	9	3^-	A-	397 039.09	3	3^+	2	2^+	A+
78 538.23	28	-7	27	-8	E	232 418.59	10	2^+	9	3^+	A+	397 041.41	3	3^-	2	2^-	A-
80 993.16	7	2^-	8	1^-	A-	232 783.50	18	3^+	17	4^+	A+	398 446.92	2	1^+	1	0^+	A+
81 653.08	18	4	19	3	E	233 795.75	18	3^-	17	4^-	A-	398 946.23	5	0	4	-1	E
82 897.08	22	5^+	23	4^+	A+	234 683.39[o]	4	2^-	5	1^-	A-						
v_t = 1 First Excited State Transitions																	
18 220.34[d]	Series Z - Line B					69 175.52	13	2^-	12	1^-	A-	134 625.06	Series Z - Line E				
21 146.74	8	2	7	3	E	69 600.20	9	2	8	3	E	186 318.93	Series Z - Line F				
27 227.11[e,q]	6	3	7	2	E	69 607.15	9	1^+	10	2^+	A+	215 302.23	6	1^+	7	2^+	A+
32 379.37[e]	Series Z - Line C					75 543.29	5	3	6	2	E	244 338.02	9	1	8	0	E
44 955.81[q]	2	0	3	1	E	76 405.14	13	2^+	12	1^+	A+	265 224.39	5	1^-	6	2^-	A-
51 509.28	5	1	4	0	E	83 320.50	Series Z - Line D					292 517.44	10	1	9	0	E
68 499.67	Series Z - Line A					118 156.5(1.0)	10	2	9	3	E						

[a] Estimated measurement accuracy is ±0.1 MHz below 200 GHz and ±0.05 MHz above 200 GHz, unless otherwise shown.

[b] Torsional symmetry (positive and negative k values for E symmetry denote respectively the E_1 and E_2 labels of Refs. 9 and 20.

[c] Reported unassigned in Ref. 8. [d] Reported unassigned in Ref. 7. [e] Reported unassigned in Ref. 3.

[f] Tentative assignment. [g] Assignment confirmed by laser-microwave double resonance in Ref. 21.

[h] Originally attributed to CH_3OD in Ref. 6, but reassigned in Refs. 1 and 9.

[i] Reported by H.D. Edwards, Ph.D. thesis, Duke University, 1950, and assigned in Ref. 9.

[j] First reported by Edwards, Gilliam and Gordy, as discussed in Refs. 4 and 5.

[k] Reported in Ref. 10. [ℓ] Reported in emission from Orion A in Ref. 11.

[m] Line erroneously reported in Ref. 9, due to incorrect identification of multiplier harmonic.

[n] Reported unassigned in Ref. 9. [o] First reported in Ref. 13. [p] Unresolved from $15_3^+ \leftarrow 15_2^-$ A v_t=0 line.

[q] Reported in Ref. 12.

for example, corresponds in reality when multiplied by 4/3 to the strong $12_{-5} \leftarrow 13_{-4}$, E, $v_t = 0$ transition at 123 782.42 MHz (*9*).

The series of "Z" lines running from Line A to Line F in the second part of Table III is clearly identifiable as part of a P branch from the relative line spacings, but has not been confidently assigned as yet. From our calculations, it is very likely the $k = 6 \leftarrow 5$, $A\pm$, $v_t = 1$, P branch, with Line A being the $J = 18 \leftarrow 19$ transition. However, this assignment of Series Z is only tentative at present, and awaits some careful Stark effect measurements at high sensitivity to attempt to confirm the J numbering.

4. DISCUSSION

In the study by Pickett *et al.* (*13*), which appeared independently while this work was in progress, frequencies for a number of the transitions in Tables I to III were reported for the first time. We decided to include our own frequencies for these transitions here for completeness and to give an idea of the experimental scatter. For most of the $v_t = 0$, ${}^QR$-branch lines in Table I, our measurements are consistent with those of Pickett *et al.* to within the estimated ±0.05-MHz accuracy, but there are significant differences in some cases. For those transitions with abnormally large (Obs-Calc) values in their tables, namely the $6_2 \leftarrow 5_2$ $A-$, $6_3 \leftarrow 5_3$ $A\pm$, $6_4 \leftarrow 5_4$ $A\pm$, $6_4 \leftarrow 5_4$ E, and $k = \pm 2$ E lines, our frequencies are in good agreement with their calculated values.

Our measurements of the $J = 8 \leftarrow 7$, $v_t = 0$, ${}^QR$-branch frequencies in Table I are also well represented by the power-series energy level expansions in $J(J + 1)$ with empirical coefficients which were given by Pickett *et al.* (*13*). However, there are substantial deviations from the predictions from their formulas at the higher J values of many of the b-type lines in Table III. For example, the $14_2 \leftarrow 13_3$, E, $v_t = 0$ transition is calculated to lie at 149 478.3 MHz using their constants, whereas the observed frequency is 147 532.59 MHz. Thus, while the predictions from the empirical power series are very valuable in locating the possible transitions from CH_3OH in a given spectral region, confident assignments of new interstellar CH_3OH lines, say, may still require backup laboratory measurements in many cases.

The $11_1 \leftarrow 10_2$ $A-$ and $5_0 \leftarrow 4_1$ E transitions included in Table III were first observed by Jennings and Fox (*11*) in emission from Orion. Their astronomically determined frequencies of 76 247.4 ± 0.4 and 76 509.9 ± 0.2 MHz, respectively, are in excellent agreement with our subsequent laboratory measurements of 76 247.27 and 76 507.67 MHz. Also, we had tentatively assigned the lines of the $k = -8 \leftarrow -7$ E P branch in Table III prior to the laser-microwave double-resonance identification by Petersen and Duxbury (*21*) of the $27_{-7} \leftarrow 26_{-8}$ member at 30 193.44 MHz. Their result provided a valuable check for the assignment of that series.

The CH_3OH frequencies have turned out to have useful astronomical applications, with productive feedback from the radio astronomers. During discussions with Dr. W. M. Irvine at the University of Massachusetts in which several initially unidentified U lines in the Onsala survey of emission toward Orion A (*15*) were identified as CH_3OH, he pointed out two other U lines as having similar characteristics. On return to the laboratory at UNB, CH_3OH lines were indeed found at those frequencies, and this led to identification of the corresponding *b*-type *P* branches in our spectra. In addition, it is virtually certain that the *U*105577 feature (*22*) observed toward the Kleinmann–Low nebula in Orion (*23*) and toward W51M (*15*) is indeed a CH_3OH line, namely the $14_{-2} \leftarrow 14_1$ transition of Table II. By $J = 14$, the lines of that *Q* branch are quite comparable in intensity to other strong methanol transitions in the same spectral region. Furthermore, lines at the $J = 15$ and $J = 16$ frequencies of the *Q* branch have also been recently observed toward Orion (*24*), supporting the identification. Finally, we note that the lines of the $J = 5 \leftarrow 4$, $v_t = 0$, ^QR-branch multiplet near 242 GHz have as well been detected in emission from Orion A (*25, 26*), with use of the measurements of Pickett *et al.* (*13*).

The present results have a number of applications to FIR and infrared studies of CH_3OH also. The measurements of the $k = 5$ and $k = 6$ *E* lines of the $J = 7 \leftarrow 6$ and $J = 8 \leftarrow 7$, $v_t = 0$, ^QR-branch multiplets in Table I are relevant to the analysis of the laser Stark spectra observed with the 337-μm HCN laser line in the FIR by Johnston *et al.* (*27*). The Stark shifts of the $k = 6 \leftarrow 5$, *E*, $v_t = 0$, *Q*-branch lines were included in that work as adjustable parameters, thus defining the line frequencies. The choice among several alternative least-squares fits to the data was then based principally on the trends of the frequency differences between the successive *Q*-branch members. From our results in Table I, the first two of these differences are now determined rigorously as

$$\nu(6_6 \leftarrow 6_5) - \nu(7_6 \leftarrow 7_5) = \nu(7_5 \leftarrow 6_5) - \nu(7_6 \leftarrow 6_6) = 70.61 \text{ MHz}$$

$$\nu(7_6 \leftarrow 7_5) - \nu(8_6 \leftarrow 8_5) = \nu(8_5 \leftarrow 7_5) - \nu(8_6 \leftarrow 7_6) = 77.2 \text{ MHz}.$$

These values compare quite well with those of 70.1 and 76.3 MHz obtained in Fit 3 of Johnston *et al.* (*27*), and provide support for the choice made of that fit as being the most plausible. It will now be possible to use the experimental *Q*-branch differences above as constraints in the fit, and perhaps reduce significantly the high correlations among parameters encountered in the laser Stark least-squares analysis.

In connection with the assignment of infrared lines in the C—O stretch band of CH_3OH, the new measurements of the ^QR-branch transitions in the $v_t = 1$ excited torsional state are proving of particular use. Due to a lack of data for $v_t = 1$ frequencies, there is uncertainty at present about the *a*-type molecular constants for the C—O stretch state (*16, 28*), and a distinct anomaly in the apparent torsional barrier height appropriate to the $v_t = 1$ levels in the C—O stretch state (*16*). Further information on these levels is thus of considerable interest. Now, the difference $[R(J - 1) - P(J + 1)]$ between infrared *R*-branch and *P*-branch transitions which terminate on the same upper level is simply the sum $[\nu(J + 1 \leftarrow J) + \nu(J \leftarrow J - 1)]$ of ground-state *a*-type rotational frequencies, so the latter can be used to establish accurate combination differences for assignment of the infrared lines. In this way, it has been possible to identify several series of $v_t = 1$ infrared lines in the diode laser spectra (*17*) and in high-resolution Fourier transform spectra of the C—O stretch band taken by Dr. J. W. C. Johns at the Herzberg Institute of Astrophysics (*29*). Analysis of the results and further assignments are in progress, and will be reported elsewhere.

For the future, there are still numerous strong CH$_3$OH lines remaining to be identified in the microwave and millimeter-wave spectra, some of which have already been detected astronomically (*24*). A fuller understanding of the spectrum would benefit from improvement of the theoretical model for the methanol Hamiltonian, and certainly from a more precise treatment of the effects of molecular asymmetry than our second-order perturbation theory approach, as the $(\nu_o - \nu_c)$ deviations in Table I are unacceptably large. Work in this direction by Herbst and DeLucia (*30*) using an extended Hamiltonian and full diagonalization of the torsion–rotation matrices gives a much better account of the spectrum, and will be reported in the near future.

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