

The Millimeter-Wave Spectrum of Methyl Mercaptan

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Approximately 400 new spectral lines of gaseous methyl mercaptan have been measured in the frequency range from 100 to 300 GHz. Most of these lines have been measured with a novel broadband millimeter-/submillimeter-wave spectrometer. A global data set consisting of our lines and approximately 200 lines determined by previous investigators has been analyzed via an internal axis method that we developed previously in the study of the spectrum of methanol. © 1986 Academic Press, Inc.

I. INTRODUCTION

Although the rotation-torsional spectrum of methyl mercaptan (CH_3SH) has not received the degree of attention accorded that of methanol (CH_3OH), it is equally dense and complex. The complexity of the methyl mercaptan spectrum is due to the internal rotation or torsion of the methyl group with respect to the hydrogen attached to the sulfur atom. The study of the effects of internal rotation on microwave spectral patterns has a long and rich history (1, 2). Essentially, two theoretical approaches have been developed to analyze complex rotation-torsional spectra—the principal axis method (PAM), which utilizes van Vleck perturbation theory to handle the rotation-torsional interaction (1–3), and the internal axis method (IAM), which utilizes a set of inertial axes in which the rotation-torsional interaction effectively disappears (2, 4, 5). We have previously (6) utilized an IAM procedure to analyze the millimeter- and submillimeter-rotation-torsional spectrum of methanol. The IAM procedure is by far the more effective of the two for light internal rotors such as CH_3OH and CH_3SH .

The first detailed laboratory studies of methyl mercaptan were undertaken by Kojima and Nishikawa (7) and Kojima (8) who studied the spectrum in the 14- to 38-GHz range. More than a decade later, Johnson (9) measured several transitions around 75 GHz. In 1979, Linke *et al.* (10) measured some additional transitions at 100 GHz and identified CH_3SH as an interstellar molecule. Interestingly, methyl mercaptan, unlike methanol, has to date only been identified in one interstellar source—Sgr B2. The most detailed rotation-torsional spectral study of CH_3SH to date has been that of Lees and Mohammadi (11). These authors carried out an investigation in the 25-

to 107-GHz region, measured and assigned about 260 new lines, and determined improved values of rotational, torsional, centrifugal distortion, and interaction constants via a nonglobal, perturbative treatment.

In this paper, we extend the study of Lees and Mohammadi (11) to a frequency of 300 GHz. Approximately 400 lines in the frequency range 100–300 GHz have been measured and assigned. These lines involve transitions between rotation–torsional energy levels with angular momentum quantum number $J \leq 10$ and torsional quantum number $v_t \leq 2$. Our measured lines have been combined with 200 lines of previous investigators and analyzed via an essentially nonperturbative diagonalization procedure involving an extended internal axis method Hamiltonian (6). Our least-squares fit to the global data set using the IAM approach has a root-mean-square deviation of 1.7 MHz, which is comparable to our previous analysis of the methanol spectrum (6), but is far worse than typical least-squares fits to the spectra of molecules that do not possess such large internal rotation effects.

II. EXPERIMENTAL DETAILS

Most of the spectral line measurements of methyl mercaptan reported here have been measured with a new broadband millimeter-/submillimeter-wave spectrometer developed at Duke University. In this system, a computer-controlled, phase-locked YIG oscillator is used to drive a 26- to 40-GHz traveling-wave tube amplifier which in turn drives a high-order harmonic generator. This system allows us to produce continuous frequency scans over large spectral regions and to record the spectra automatically. The system is particularly advantageous for molecules such as methyl mercaptan which possess complex spectra, and which would require large amounts of time for spectral measurement on a standard klystron-based spectrometer. A detailed description of this spectrometer is currently being written (12). The lower frequency lines (100–125 GHz) reported here have been measured with a klystron-based spectrometer at the University of New Brunswick.

III. THEORY

The internal axis method employed here has been described in detail in our previous paper on methanol (6) and is only discussed briefly. The Hamiltonian utilized, tabulated in Table I of Ref. (6), follows that of Lees and Baker in their classic early study of methanol (5). This Hamiltonian is divided into three terms which describe the overall rotation of the molecule, the torsional motion of the methyl group, and the distortion and interaction among the assorted angular momentum and torsional potential terms. The basis set used to evaluate the Hamiltonian can be written as

$$|JKv_t\sigma\rangle = |JK\rangle|Kv_t\sigma\rangle \quad (1)$$

where J is the overall angular momentum quantum number (with associated operator P), K is the quantum number of the angular momentum projection on the a inertial axis of the molecule (with associated operator P_a), v_t is the torsional (vibrational) quantum number, and σ is a parameter which describes the torsional substates of A ($\sigma = 0$) and E ($\sigma = \pm 1$) symmetries. The eigenvectors $|Kv_t\sigma\rangle$ derive from a diagonalization of the torsional part of the Hamiltonian utilizing as a basis the product of free

rotor eigenfunctions of P_γ for the torsional motion, where γ is the torsional angle, and eigenfunctions $|K\rangle$ of P_a . The free rotor eigenfunctions of P_γ can be written as

$$|k\sigma\rangle = (1/2\pi)^{1/2} \exp[i(3k + \sigma)\gamma] \quad (2)$$

where k is any integer and the quantum number σ derives from the symmetry of the methyl group. It was found that diagonalization of the torsional Hamiltonian for each value of σ and K results in sufficiently accurate torsional eigenvectors and eigenvalues if a 21×21 matrix ($-10 \leq k \leq 10$) is utilized.

Once the $|Kv_t\sigma\rangle$ basis functions are determined, the matrix elements of the total Hamiltonian can be written down. These matrix elements are listed in Table II of Ref. (6). In this work, two additional terms in the distortion-interaction part of the Hamiltonian have been added. These terms, labeled H_1 and H_2 , are listed in Table I along with their matrix elements. They have been added to account more properly for the change in the rotation constant D_{ab} with torsional state and for the variation

TABLE I

Additional Matrix Elements of Rotation-Torsional Hamiltonian^a

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

$$|Kv_t\sigma\rangle = (1/2\pi)^{1/2} |K\rangle \sum_{k=-10}^{+10} A_{3k+\sigma}^{K,v} \exp[i(3k+\sigma)\gamma]$$

$\sigma = 0$ (A) $\sigma = 1, -1$ (E)

New Terms in Hamiltonian

$$H_1 = d_{ab} (P_a P_b + P_b P_a) (1 - \cos 3\gamma)$$

$$H_2 = 1_v P_a^2 P_a^3 (P_\gamma + \rho P_a)$$

Matrix Elements

$$\langle JKv_t\sigma | H_1 | J K \pm 1 v_t \sigma \rangle = d_{ab} [J(J+1) - K(K\pm 1)]^{1/2} (K \pm 1/2)$$

$$\times \sum_k [A_{3k+\sigma}^{K,v} A_{3k+\sigma}^{K\pm 1,v} - 0.5 (A_{3(k+1)+\sigma}^{K,v} A_{3k+\sigma}^{K\pm 1,v} + A_{3k+\sigma}^{K,v} A_{3(k+1)+\sigma}^{K\pm 1,v})]$$

$$\langle JKv_t\sigma | H_2 | JKv_t\sigma \rangle = 1_v J(J+1) K^3 \sum_k (A_{3k+\sigma}^{K,v})^2 (3k+\sigma+\rho K)$$

^a The subscript t of the torsional quantum number is omitted in selected expressions for clarity. The parameter ρ in H_2 is defined in (5).

TABLE II
Methyl Mercaptan A Transitions

VTOR	SIGMA	J'	K'	P'	←	J''	K''	P''	FREQUENCY(MHZ)	RESIDUAL(MHZ)	REFERENCE
0	0	1	1	-	←	1	0	+	105998.470	-0.872	a
0	0	1	0	+	←	0	0	+	25290.900	0.075	a
1	0	1	0	+	←	0	0	+	25219.510	-0.340	a
2	0	1	0	+	←	0	0	+	25143.560	0.165	a
0	0	2	1	-	←	2	0	+	106524.130	-1.075	a
0	0	2	2	-	←	2	1	+	293511.937	-0.928	
0	0	2	2	+	←	2	1	-	291944.672	-0.588	
1	0	2	1	+	←	2	2	-	60259.140	4.287	a
1	0	2	1	-	←	2	2	+	61289.200	4.805	a
0	0	2	0	+	←	1	0	+	50579.330	0.121	a
0	0	2	1	+	←	1	1	+	50058.890	0.248	a
0	0	2	1	-	←	1	1	-	51104.980	-0.093	a
1	0	2	0	+	←	1	0	+	50440.430	-0.701	a
1	0	2	1	+	←	1	1	+	50080.230	-1.090	a
1	0	2	1	-	←	1	1	-	50765.560	-0.908	a
2	0	2	0	+	←	1	0	+	50286.650	0.351	a
2	0	2	1	+	←	1	1	+	49930.180	0.055	a
2	0	2	1	-	←	1	1	-	50670.720	0.199	a
0	0	2	0	+	←	1	1	+	-54895.960	0.938	a
0	0	3	1	-	←	3	0	+	107316.460	-1.224	a
0	0	3	2	-	←	3	1	+	294298.441	-0.897	
0	0	3	2	+	←	3	1	-	291169.989	-0.438	
1	0	3	1	+	←	3	2	-	59769.140	3.157	a
1	0	3	1	-	←	3	2	+	61834.300	3.998	a
0	0	3	0	+	←	2	0	+	75862.870	0.157	b
0	0	3	1	+	←	2	1	+	75085.910	0.263	a
0	0	3	1	-	←	2	1	-	76655.180	-0.012	a
0	0	3	2	+	←	2	2	+	75880.490	0.131	b
0	0	3	2	-	←	2	2	-	75872.320	0.200	b
1	0	3	0	+	←	2	0	+	75664.210	-1.059	a
1	0	3	1	+	←	2	1	+	75117.490	-1.700	a
1	0	3	1	-	←	2	1	-	76145.490	-1.291	a
1	0	3	2	+	←	2	2	+	75600.380	-0.494	a
1	0	3	2	-	←	2	2	-	75607.780	-0.279	a
2	0	3	0	+	←	2	0	+	75428.810	0.590	a
2	0	3	1	+	←	2	1	+	74894.240	0.004	a
2	0	3	1	-	←	2	1	-	76005.210	0.449	a
2	0	3	2	+	←	2	2	+	75474.460	0.429	a
2	0	3	2	-	←	2	2	-	75474.460	0.985	a
0	0	3	1	+	←	2	0	+	180041.085	-0.103	
0	0	3	0	+	←	2	1	+	-29091.900	0.928	c
1	0	3	2	+	←	2	1	+	15339.000	-5.224	d
1	0	3	2	-	←	2	1	-	14320.200	-5.261	d
0	0	4	1	-	←	4	0	+	108379.780	-1.412	
0	0	4	2	-	←	4	1	+	295347.250	-1.295	
0	0	4	2	+	←	4	1	-	290147.226	-0.479	
1	0	4	1	+	←	4	2	-	59113.620	1.730	a
1	0	4	1	-	←	4	2	+	62567.060	3.040	a
0	0	4	0	+	←	3	0	+	101139.160	0.263	e
0	0	4	1	+	←	3	1	+	100110.270	0.388	e, a
0	0	4	1	-	←	3	1	-	102202.490	0.086	e, a
0	0	4	2	+	←	3	2	+	101179.760	0.078	a
0	0	4	2	-	←	3	2	-	101159.460	0.370	a
0	0	4	3	+	←	3	3	+	101160.530	0.150	a
0	0	4	3	-	←	3	3	-	101160.530	0.114	a

^a Lees and Mohammadi (11).

^b Johnson (9).

^c Kojima and Nishikawa (7).

^d Kojima (8).

^e Linke et al. (10).

TABLE II—Continued

VTOR	SIGMA	J'	K'	P'	←	J''	K''	P''	FREQUENCY(MHZ)	RESIDUAL(MHZ)	REFERENCE
1	0	4	0	+	←	3	0	+	100892.190	-1.497	a
1	0	4	1	+	←	3	1	+	100151.450	-2.271	a
1	0	4	1	-	←	3	1	-	101521.750	-1.832	a
1	0	4	2	+	←	3	2	+	100789.200	-0.664	a
1	0	4	2	-	←	3	2	-	100807.000	-0.813	a
1	0	4	3	+	←	3	3	+	100818.040	-2.344	a
1	0	4	3	-	←	3	3	-	100818.040	-2.393	a
2	0	4	0	+	←	3	0	+	100569.480	0.812	a
2	0	4	1	+	←	3	1	+	99857.170	-0.034	a
2	0	4	1	-	←	3	1	-	101338.270	0.495	a
2	0	4	2	+	←	3	2	+	100631.690	0.748	a
2	0	4	2	-	←	3	2	-	100630.670	1.118	a
2	0	4	3	+	←	3	3	+	100613.220	1.059	a
2	0	4	3	-	←	3	3	-	100613.220	1.059	a
0	0	4	1	+	←	3	0	+	204287.938	-0.419	
1	0	4	2	+	←	3	1	+	410111.080	-3.818	a
1	0	4	2	-	←	3	1	-	38981.600	-4.894	a
0	0	5	1	-	←	5	0	+	109720.003	-1.584	
0	0	5	1	-	←	5	1	+	7846.000	-1.019	c
0	0	5	2	-	←	5	1	+	296659.887	-1.077	
1	0	5	1	+	←	5	2	-	58290.630	-0.034	a
1	0	5	1	-	←	5	2	+	63492.080	1.561	a
0	0	5	0	+	←	4	0	+	126405.679	0.348	
0	0	5	1	+	←	4	1	+	125130.914	0.476	
0	0	5	2	+	←	4	2	+	126484.160	0.131	
0	0	5	2	-	←	4	2	-	126443.252	0.395	
0	0	5	3	+	←	4	3	+	126449.760	0.507	
0	0	5	3	-	←	4	3	-	126449.760	0.380	
0	0	5	4	+	←	4	4	+	126436.214	0.218	
0	0	5	4	-	←	4	4	-	126436.214	0.218	
1	0	5	0	+	←	4	0	+	126125.806	-1.988	
1	0	5	1	+	←	4	1	+	125181.184	-2.636	
1	0	5	1	-	←	4	1	-	126893.480	-2.207	
1	0	5	2	+	←	4	2	+	125968.474	-0.714	
1	0	5	2	-	←	4	2	-	126004.083	-0.964	
1	0	5	3	+	←	4	3	+	126024.539	-2.285	
1	0	5	3	-	←	4	3	-	126024.539	-2.454	
1	0	5	4	+	←	4	4	+	126049.955	-2.636	
1	0	5	4	-	←	4	4	-	126049.955	-2.636	
2	0	5	0	+	←	4	0	+	125708.185	1.032	
2	0	5	1	+	←	4	1	+	124818.712	0.062	
2	0	5	1	-	←	4	1	-	126669.682	0.526	
2	0	5	2	+	←	4	2	+	125788.072	1.163	
2	0	5	2	-	←	4	2	-	125785.287	1.157	
2	0	5	3	+	←	4	3	+	125770.308	1.255	
2	0	5	3	-	←	4	3	-	125770.308	1.255	
0	0	5	1	+	←	4	0	+	228279.569	-0.330	
0	0	5	0	+	←	4	1	+	23256.900	1.030	c
1	0	5	2	+	←	4	1	+	66828.120	-2.246	a
1	0	5	2	-	←	4	1	-	63463.950	-4.008	a
0	0	6	1	-	←	6	0	+	111344.346	-1.812	
0	0	6	1	-	←	6	1	+	10983.400	-1.362	c
0	0	6	2	-	←	6	1	+	298236.059	-1.106	
0	0	6	2	+	←	6	1	-	287396.029	-0.457	
1	0	6	1	+	←	6	2	-	57298.020	-1.930	a
1	0	6	1	-	←	6	2	+	64615.720	-0.235	a
0	0	6	0	+	←	5	0	+	151660.039	0.447	
0	0	6	1	+	←	5	1	+	150146.630	0.211	
0	0	6	1	-	←	5	1	-	153284.423	0.260	
0	0	6	2	+	←	5	2	+	151794.863	0.223	
0	0	6	2	-	←	5	2	-	151723.140	0.519	
0	0	6	3	+	←	5	3	+	151737.906	0.629	
0	0	6	3	-	←	5	3	-	151737.906	0.290	
0	0	6	4	+	←	5	4	+	151720.699	0.292	
0	0	6	4	-	←	5	4	-	151720.699	0.281	
0	0	6	5	+	←	5	5	+	151706.308	-0.072	
0	0	6	5	-	←	5	5	-	151706.308	-0.072	

TABLE II—Continued

VTOR	SIGMA	J'	K'	P'	←	J''	K''	P''	FREQUENCY(MHZ)	RESIDUAL(MHZ)	REFERENCE
1	0	6	0	+	←	5	0	+	151366.454	-2.527	
1	0	6	1	+	←	5	1	+	150205.077	-3.333	
1	0	6	1	-	←	5	1	-	152259.325	-2.575	
1	0	6	2	+	←	5	2	+	151135.644	-0.820	
1	0	6	2	-	←	5	2	-	151198.007	-1.117	
1	0	6	3	+	←	5	3	+	151230.615	-3.499	
1	0	6	3	-	←	5	3	-	151230.615	-3.950	
1	0	6	4	+	←	5	4	+	151258.007	-1.317	
1	0	6	4	-	←	5	4	-	151258.007	-1.317	
2	0	6	0	+	←	5	0	+	150844.237	1.054	
2	0	6	1	-	←	5	1	-	151998.964	0.469	
2	0	6	2	+	←	5	2	+	150943.212	1.516	
2	0	6	2	-	←	5	2	-	150938.378	1.543	
2	0	6	3	+	←	5	3	+	150929.784	1.287	
2	0	6	3	-	←	5	3	-	150929.784	1.287	
0	0	6	1	+	←	5	0	+	252021.034	0.046	
0	0	6	0	+	←	5	1	+	49786.080	1.056	a
1	0	6	2	+	←	5	1	+	92782.700	-0.310	a
1	0	6	2	-	←	5	1	-	87768.270	-3.125	a
0	0	7	1	-	←	7	0	+	113261.614	-1.974	
0	0	7	1	-	←	7	1	+	14643.100	-1.423	c
0	0	7	2	-	←	7	1	+	300076.884	-0.920	
0	0	7	2	+	←	7	1	-	285691.859	-0.657	
1	0	7	1	+	←	7	2	-	56133.150	-3.830	a
1	0	7	1	-	←	7	2	+	65945.150	-2.476	a
0	0	7	0	+	←	6	0	+	176899.853	0.577	
0	0	7	1	+	←	6	1	+	175157.480	0.534	
0	0	7	1	-	←	6	1	-	178817.138	0.431	
0	0	7	2	+	←	6	2	+	177112.939	0.201	
0	0	7	2	-	←	6	2	-	176998.486	0.902	
0	0	7	3	+	←	6	3	+	177025.048	0.799	
0	0	7	3	-	←	6	3	-	177025.048	0.037	
0	0	7	4	+	←	6	4	+	177003.710	0.388	
0	0	7	4	-	←	6	4	-	177003.710	0.390	
0	0	7	5	+	←	6	5	+	176986.132	-0.057	
0	0	7	5	-	←	6	5	-	176986.132	-0.057	
0	0	7	6	+	←	6	6	+	176973.388	0.007	
0	0	7	6	-	←	6	6	-	176973.388	0.007	
1	0	7	0	+	←	6	0	+	176615.624	-2.983	
1	0	7	1	+	←	6	1	+	175223.066	-3.368	
1	0	7	1	-	←	6	1	-	177618.114	-2.897	
1	0	7	2	+	←	6	2	+	176288.603	-0.738	
1	0	7	2	-	←	6	2	-	176387.724	-1.680	
1	0	7	3	+	←	6	3	+	176438.749	-3.631	
1	0	7	3	-	←	6	3	-	176438.749	-4.645	
1	0	7	4	+	←	6	4	+	176462.216	-1.776	
1	0	7	4	-	←	6	4	-	176462.216	-1.775	
2	0	7	0	+	←	6	0	+	175977.431	1.162	
2	0	7	1	+	←	6	1	+	174735.790	0.338	
2	0	7	1	-	←	6	1	-	177325.927	0.545	
2	0	7	2	+	←	6	2	+	176096.777	1.710	
2	0	7	2	-	←	6	2	-	176088.915	1.623	
2	0	7	3	+	←	6	3	+	176091.747	0.757	
2	0	7	3	-	←	6	3	-	176091.747	0.757	
0	0	7	1	+	←	6	0	+	275518.407	0.065	
0	0	7	0	+	←	6	1	+	76539.020	1.140	a
0	0	8	1	-	←	8	0	+	115481.799	-2.115	
0	0	8	1	-	←	8	1	+	18824.200	-1.499	c
0	0	8	2	-	←	8	1	+	302183.140	-0.456	
0	0	8	2	+	←	8	1	-	283788.715	-0.988	
1	0	8	1	+	←	8	2	-	54792.750	-5.846	a
1	0	8	1	-	←	8	2	+	67488.720	-5.181	a
0	0	8	0	+	←	7	0	+	202122.763	0.755	
0	0	8	1	+	←	7	1	+	200161.913	0.757	
0	0	8	1	-	←	7	1	-	204342.948	0.615	
0	0	8	2	+	←	7	2	+	202439.833	0.313	
0	0	8	2	-	←	7	2	-	202268.173	1.224	

TABLE II—Continued

VTOR	SIGMA	J'	K'	P'	←	J''	K''	P''	FREQUENCY(MHZ)	RESIDUAL(MHZ)	REFERENCE
0	0	8	3	+	←	7	3	+	202310.937	0.989	
0	0	8	3	-	←	7	3	-	202312.295	0.825	
0	0	8	4	+	←	7	4	+	202285.068	0.610	
0	0	8	4	-	←	7	4	-	202285.068	0.615	
0	0	8	5	+	←	7	5	+	202264.023	0.142	
0	0	8	5	-	←	7	5	-	202264.023	0.142	
0	0	8	6	+	←	7	6	+	202248.642	0.220	
0	0	8	6	-	←	7	6	-	202248.642	0.220	
0	0	8	7	+	←	7	7	+	202230.077	0.110	
0	0	8	7	-	←	7	7	-	202230.077	0.110	
1	0	8	0	+	←	7	0	+	201874.266	-3.720	
1	0	8	1	+	←	7	1	+	200233.348	-3.512	
1	0	8	1	-	←	7	1	-	202968.505	-3.286	
1	0	8	2	+	←	7	2	+	201425.047	-0.469	
1	0	8	2	-	←	7	2	-	201573.680	-1.563	
1	0	8	3	+	←	7	3	+	201646.434	-5.285	
1	0	8	3	-	←	7	3	-	201648.582	-5.165	
1	0	8	4	+	←	7	4	+	201662.450	-3.799	
1	0	8	4	-	←	7	4	-	201662.450	-3.798	
2	0	8	0	+	←	7	0	+	201107.176	1.255	
2	0	8	1	+	←	7	1	+	199690.575	0.526	
2	0	8	1	-	←	7	1	-	202649.950	0.540	
2	0	8	2	+	←	7	2	+	201248.778	1.994	
2	0	8	2	-	←	7	2	-	201237.108	1.982	
2	0	8	3	+	←	7	3	+	201257.421	0.410	
2	0	8	3	-	←	7	3	-	201257.421	0.409	
0	0	8	1	+	←	7	0	+	298780.424	0.202	
0	0	8	0	+	←	7	1	+	103504.340	1.398	a
0	0	8	1	+	←	7	2	+	-100173.000	2.883	a
0	0	8	1	-	←	7	2	-	-81090.900	0.048	a
0	0	9	1	-	←	9	0	+	118016.331	-2.126	
0	0	9	1	-	←	9	1	+	23526.200	-1.283	c
0	0	9	2	-	←	9	1	+	304555.795	0.493	
0	0	9	2	+	←	9	1	-	281704.296	-1.553	
1	0	9	1	+	←	9	2	-	53273.670	-7.615	a
1	0	9	1	-	←	9	2	+	69255.730	-8.402	a
0	0	9	0	+	←	8	0	+	227326.392	0.941	
0	0	9	1	+	←	8	1	+	225158.984	0.773	
0	0	9	1	-	←	8	1	-	229860.995	1.000	
0	0	9	2	+	←	8	2	+	227776.513	0.373	
0	0	9	2	-	←	8	2	-	227531.445	1.528	
0	0	9	3	+	←	8	3	+	227595.057	0.927	
0	0	9	3	-	←	8	3	-	227598.158	1.239	
0	0	9	4	+	←	8	4	+	227564.379	0.805	
0	0	9	4	-	←	8	4	-	227564.379	0.818	
0	0	9	5	+	←	8	5	+	227539.453	0.302	
0	0	9	5	-	←	8	5	-	227539.453	0.302	
0	0	9	6	+	←	8	6	+	227521.215	0.499	
0	0	9	6	-	←	8	6	-	227521.215	0.499	
0	0	9	7	+	←	8	7	+	227499.477	0.322	
0	0	9	7	-	←	8	7	-	227499.477	0.322	
0	0	9	8	+	←	8	8	+	227465.717	-1.108	
0	0	9	8	-	←	8	8	-	227465.717	-1.108	
1	0	9	0	+	←	8	0	+	227143.964	-4.396	
1	0	9	1	+	←	8	1	+	225235.146	-3.537	
1	0	9	1	-	←	8	1	-	228309.423	-3.567	
1	0	9	2	+	←	8	2	+	226542.333	-0.426	
1	0	9	2	-	←	8	2	-	226754.247	-1.747	
1	0	9	3	+	←	8	3	+	226855.566	-6.637	
1	0	9	3	-	←	8	3	-	226861.620	-4.297	
1	0	9	4	+	←	8	4	+	226861.620	-4.131	
1	0	9	4	-	←	8	4	-	226861.620	-4.127	
2	0	9	0	+	←	8	0	+	226233.300	1.650	
2	0	9	1	+	←	8	1	+	224642.333	0.729	
2	0	9	1	-	←	8	1	-	227970.556	0.388	
2	0	9	2	+	←	8	2	+	226398.730	2.120	
2	0	9	2	-	←	8	2	-	226382.079	2.115	
2	0	9	3	+	←	8	3	+	226426.757	-0.269	
2	0	9	3	-	←	8	3	-	226426.757	-0.271	
0	0	9	1	+	←	8	0	+	321816.713	0.288	
0	0	9	1	+	←	8	2	+	-77453.860	3.332	a
0	0	9	1	-	←	8	2	-	-53498.110	-0.208	a

TABLE II—Continued

VTOR	SIGMA	J'	K'	P'	←	J''	K''	P''	FREQUENCY(MHZ)	RESIDUAL(MHZ)	REFERENCE
0	0	10	1	-	←	10	0	+	120877.901	-1.847	
0	0	10	1	-	←	10	1	+	28747.900	-0.912	c
0	0	10	2	-	←	10	1	+	307195.399	1.696	
0	0	10	2	+	←	10	1	-	279458.568	-2.353	
1	0	10	1	+	←	10	2	-	51572.080	-9.133	a
1	0	10	1	-	←	10	2	+	71256.230	-12.302	a
0	0	10	0	+	←	9	0	+	252508.348	1.016	
0	0	10	1	+	←	9	1	+	250148.094	0.800	
0	0	10	1	-	←	9	1	-	255369.920	1.297	
0	0	10	2	+	←	9	2	+	253124.169	0.474	
0	0	10	2	-	←	9	2	-	252787.694	1.999	
0	0	10	3	+	←	9	3	+	252878.153	1.624	
0	0	10	3	-	←	9	3	-	252882.612	1.304	
0	0	10	4	+	←	9	4	+	252841.551	1.135	
0	0	10	4	-	←	9	4	-	252841.551	1.162	
0	0	10	5	+	←	9	5	+	252812.254	0.557	
0	0	10	5	-	←	9	5	-	252812.254	0.557	
0	0	10	6	+	←	9	6	+	252790.575	0.659	
0	0	10	6	-	←	9	6	-	252790.575	0.659	
0	0	10	7	+	←	9	7	+	252765.868	0.899	
0	0	10	7	-	←	9	7	-	252765.868	0.899	
0	0	10	8	+	←	9	8	+	252727.880	-0.658	
0	0	10	8	-	←	9	8	-	252727.880	-0.658	
0	0	10	9	+	←	9	9	+	252684.033	-1.554	
0	0	10	9	-	←	9	9	-	252684.033	-1.554	
1	0	10	0	+	←	9	0	+	252425.780	-5.099	
1	0	10	1	+	←	9	1	+	250227.489	-3.447	
1	0	10	1	-	←	9	1	-	253639.403	-3.930	
1	0	10	2	+	←	9	2	+	251638.963	0.030	
1	0	10	2	-	←	9	2	-	251929.051	-1.957	
1	0	10	3	+	←	9	3	+	252067.088	-6.779	
1	0	10	3	-	←	9	3	-	252073.241	-6.987	
1	0	10	4	+	←	9	4	+	252057.713	-4.439	
1	0	10	4	-	←	9	4	-	252057.713	-4.431	
2	0	10	0	+	←	9	0	+	251354.637	1.669	
2	0	10	1	-	←	9	1	-	253287.450	0.202	
2	0	10	2	+	←	9	2	+	251546.532	2.226	
2	0	10	2	-	←	9	2	-	251523.631	2.202	
2	0	10	3	+	←	9	3	+	251600.096	-1.378	
2	0	10	3	-	←	9	3	-	251600.096	-1.381	
0	0	10	1	+	←	9	2	+	-55082.310	3.728	a
0	0	10	1	-	←	9	2	-	-25659.700	-0.503	c

in K dependence of a -type transitions in different torsional states. Their inclusion results in only a small improvement in our analysis of methyl mercaptan but is indispensable to our analysis of the acetaldehyde rotation-torsional spectrum (13).

A direct diagonalization procedure has been utilized to determine the overall rotation-torsional eigenvalues and eigenfunctions (6). Matrix elements connecting $\Delta v_t = 0, \pm 1$, and ± 2 have been included, although the off-diagonal matrix elements of selected interaction constants have not been utilized (6). Inclusion of these elements has been attempted for selected cases and apparently found not to be useful.

The diagonalized rotation-torsional states are not classified according to standard asymmetric top terminology $|JK_{-1}K_{+1}v_t\sigma\rangle$ because methyl mercaptan, like methanol, is a near-prolate symmetric top. Instead, the E levels are described by the basis set quantum numbers $|JKv_t\sigma = 1\rangle$ where $-J \leq K \leq J$ and the A levels are described by linear combinations of these quantum numbers $|JKv_t\sigma = 0\rangle \pm (-1)^K |J, -K, v_t\sigma = 0\rangle$ ($K > 0$) referred to as + and - parities although the + and - designations are not total parity quantum numbers (5). Strongly allowed transitions with this description

of the eigenfunctions are given in the literature (5, 6). These transitions can be divided into several major groupings: *a*-type *R*-branch transitions ($\Delta J = 1, \Delta K = 0$), *b*-type *Q*-branch transitions ($\Delta J = 0, \Delta K = \pm 1$), *b*-type *R*- and *P*-branch transitions ($\Delta J = \pm 1, \Delta K = 1$), and *K*-doubling transitions ($\Delta J = \Delta K = 0, + \leftrightarrow -$). In our analysis we have included 612 transitions of these types involving $J \leq 10$ and $v_t \leq 2$. Assignments have been checked carefully with combination relations and error curve techniques. (Error curves are plots of the observed minus calculated frequencies vs quantum numbers for a series of analogous transitions.) Indeed, the necessity of utilizing error curve relations, caused by the relatively poor quality of the fit to the data and the density of the spectrum, prompted the measurement and analysis of a much larger number of lines than is generally needed to model normal asymmetric rotors. Previous investigators have assigned some lines with $v_t = 3$ and values of J significantly higher than 10 [see, e.g., Reference (11)]. However, our direct diagonalization procedure becomes unwieldy and time consuming if overly large matrices are utilized, as is required if higher values of J and v_t are to be included in the analysis. In addition, our measurement of strong *a*-type transitions only involves values of J up to 10, and we have experienced difficulty in assigning transitions with high torsional quantum numbers. Our analysis has been accomplished with a nonlinear least-squares program which fits the entire spectrum based on the IAM matrix elements discussed above and in Ref. (6).

IV. RESULTS

All lines fit by our analysis are included in Table II (*A* symmetry species) and Table III (*E* symmetry species) in which frequencies, quantum assignments, residuals, and references to investigators other than ourselves are listed. Uncertainties in the frequencies measured in this work have been estimated to be ± 50 kHz. Other uncertainties are as determined by the original investigators. The root-mean-square deviation of the fit has been determined to be 1.7 MHz by varying 21 parameters; the values of these parameters ("constants") are shown in Table IV along with previously obtained values. These parameters are all defined in Ref. (6) with the exception of d_{ab} and l_v which are shown in Table I. All the other 34 parameters defined in (6) have been set to zero. Exclusion of the constants d_{ab} and l_v results in a somewhat worse fit with root-mean-square deviation 2.0 MHz. Many of our rotation, torsion, distortion, and interaction constants agree reasonably well with previously determined values although earlier studies have not utilized the number of constants used here. There are some exceptions to this agreement, due mainly to our use of a more complete set of distortion and interaction constants which correlate to some extent with the rotation and torsion parameters and in some instances change the meaning of these constants. As an example, consider the rotation constant D_{ab} , which arises in the IAM treatment because the principal axis system of the molecule is not utilized. Our value for this constant is almost double the previous value of Lees and Mohammadi (11). The reason for this discrepancy is our use of the interaction constant d_{ab} because the matrix elements of the term involving this constant occupy the same places in the Hamiltonian matrix as do those of D_{ab} . Indeed, the d_{ab} term represents an attempt to include the torsional dependence of D_{ab} . Thus, our D_{ab} is not exactly comparable to that determined by

TABLE III
Methyl Mercaptan *E* Transitions

VTOR	SIGMA	J'	K'	P'	←	J''	K''	P''	FREQUENCY(MHZ)	RESIDUAL(MHZ)	REFERENCE
0	1	1	-1	←	←	1	0	←	65345.600	-3.583	a
0	1	1	1	←	←	1	0	←	99185.080	2.705	a
1	1	1	0	←	←	1	1	←	31989.580	1.063	b
0	1	1	0	←	←	0	0	←	25291.790	0.011	a
1	1	1	0	←	←	0	0	←	25206.860	-0.457	a
2	1	1	0	←	←	0	0	←	25154.930	0.349	a
0	1	1	-1	←	←	0	0	←	90637.440	-3.522	a
0	1	2	-2	←	←	2	-1	←	269147.081	1.804	a
0	1	2	-1	←	←	2	0	←	65330.270	-3.553	a
0	1	2	1	←	←	2	0	←	99203.460	2.687	a
0	1	2	2	←	←	2	1	←	248886.513	0.205	a
1	1	2	0	←	←	2	1	←	31994.740	0.893	b
0	1	2	-1	←	←	1	-1	←	50565.590	0.165	a
0	1	2	0	←	←	1	0	←	50580.870	0.085	a
0	1	2	1	←	←	1	1	←	50599.330	0.146	a
1	1	2	-1	←	←	1	-1	←	50431.330	-1.081	a
1	1	2	0	←	←	1	0	←	50412.380	-0.968	a
1	1	2	1	←	←	1	1	←	50407.260	-0.757	a
2	1	2	-1	←	←	1	-1	←	50292.650	0.709	a
2	1	2	0	←	←	1	0	←	50309.500	0.534	a
2	1	2	1	←	←	1	1	←	50322.970	0.951	a
0	1	2	0	←	←	1	-1	←	-14764.500	3.898	c
0	1	2	0	←	←	1	1	←	-48604.110	-2.521	a
1	1	2	1	←	←	1	0	←	18417.600	-1.900	b
1	1	2	0	←	←	1	1	←	82402.060	0.196	a
0	1	3	-2	←	←	3	-1	←	269204.492	1.801	a
0	1	3	-1	←	←	3	0	←	65282.260	-3.569	a
0	1	3	1	←	←	3	0	←	99264.980	2.689	a
0	1	3	2	←	←	3	1	←	248835.341	0.060	a
1	1	3	-3	←	←	3	-2	←	32819.240	-3.951	b
1	1	3	0	←	←	3	1	←	32002.230	0.656	b
0	1	3	-2	←	←	2	-2	←	75873.810	0.142	d
0	1	3	-1	←	←	2	-1	←	75816.450	0.196	a
0	1	3	0	←	←	2	0	←	75864.430	0.182	d
0	1	3	1	←	←	2	1	←	75925.910	0.144	a
0	1	3	2	←	←	2	2	←	75874.980	0.242	d
1	1	3	-2	←	←	2	-2	←	75632.830	-0.989	a
1	1	3	-1	←	←	2	-1	←	75645.970	-1.553	a
1	1	3	0	←	←	2	0	←	75615.410	-1.395	a
1	1	3	1	←	←	2	1	←	75607.780	-1.298	a
1	1	3	2	←	←	2	2	←	75628.340	-1.708	a
2	1	3	-2	←	←	2	-2	←	75432.150	0.053	a
2	1	3	-1	←	←	2	-1	←	75437.730	1.081	a
2	1	3	0	←	←	2	0	←	75463.760	0.801	a
2	1	3	1	←	←	2	1	←	75483.770	1.423	a
2	1	3	2	←	←	2	2	←	75452.080	1.244	a
0	1	3	1	←	←	2	0	←	175129.501	2.962	a
0	1	3	0	←	←	2	1	←	-23339.200	-2.675	c
1	1	3	1	←	←	2	0	←	43613.160	-2.071	a
0	1	4	-2	←	←	4	-1	←	269342.080	1.806	a
0	1	4	-1	←	←	4	0	←	65172.430	-3.423	a
0	1	4	1	←	←	4	0	←	99409.740	2.710	a
0	1	4	2	←	←	4	1	←	248719.374	0.243	a
1	1	4	-3	←	←	4	-2	←	32820.710	-3.204	b
1	1	4	0	←	←	4	1	←	32011.700	0.327	b
0	1	4	-3	←	←	3	-3	←	101160.530	0.609	a
0	1	4	-2	←	←	3	-2	←	101167.150	0.144	e, a

^a Lees and Mohammadi (11).

^b Kojima (8).

^c Kojima and Nishikawa (7).

^d Johnson (9).

^e Linke et al. (10).

TABLE III—Continued

VTOR	SIGMA	J'	K'	P'	←	J''	K''	P''	FREQUENCY(MHZ)	RESIDUAL(MHZ)	REFERENCE
0	1	4	-1	←	←	3	-1	←	101029.750	0.328	a, a
0	1	4	0	←	←	3	0	←	101139.650	0.251	e
0	1	4	1	←	←	3	1	←	101284.360	0.222	a, a
0	1	4	2	←	←	3	2	←	101168.340	0.352	a, a
0	1	4	3	←	←	3	3	←	101156.860	0.135	a
1	1	4	-3	←	←	3	-3	←	100841.610	-0.572	a
1	1	4	-2	←	←	3	-2	←	100840.100	-1.359	a
1	1	4	-1	←	←	3	-1	←	100859.270	-2.052	a
1	1	4	0	←	←	3	0	←	100814.540	-1.863	a
1	1	4	1	←	←	3	1	←	100805.050	-1.554	a
1	1	4	2	←	←	3	2	←	100837.990	-2.287	a
1	1	4	3	←	←	3	3	←	100863.300	-2.293	a
2	1	4	-3	←	←	3	-3	←	100602.120	1.512	a
2	1	4	-2	←	←	3	-2	←	100573.490	0.076	a
2	1	4	-1	←	←	3	-1	←	100581.310	1.468	a
2	1	4	0	←	←	3	0	←	100617.360	0.997	a
2	1	4	1	←	←	3	1	←	100643.710	1.851	a
2	1	4	2	←	←	3	2	←	100599.830	1.739	a
2	1	4	3	←	←	3	3	←	100562.550	0.878	a
0	1	4	0	←	←	3	-1	←	35857.400	3.831	b
0	1	4	1	←	←	3	0	←	200549.686	3.257	
1	1	4	1	←	←	3	0	←	68802.610	-2.420	a
0	1	5	-2	←	←	5	-1	←	269609.638	1.426	
0	1	5	-1	←	←	5	0	←	64963.470	-3.070	a
0	1	5	1	←	←	5	0	←	99689.290	2.625	a
0	1	5	2	←	←	5	1	←	248499.052	0.317	
1	1	5	-3	←	←	5	-2	←	32827.910	-2.244	b
1	1	5	0	←	←	5	1	←	32022.710	-0.103	b
0	1	5	-4	←	←	4	-4	←	126441.214	0.209	
0	1	5	-3	←	←	4	-3	←	126449.760	0.866	
0	1	5	-2	←	←	4	-2	←	126462.329	0.228	
0	1	5	-1	←	←	4	-1	←	126194.649	0.485	
0	1	5	0	←	←	4	0	←	126403.967	0.491	
0	1	5	1	←	←	4	1	←	126683.350	0.240	
0	1	5	2	←	←	4	2	←	126463.155	0.440	
0	1	5	3	←	←	4	3	←	126445.428	0.181	
0	1	5	4	←	←	4	4	←	126436.936	0.045	
1	1	5	-3	←	←	4	-3	←	126051.649	-0.585	
1	1	5	-2	←	←	4	-2	←	126044.430	-1.564	
1	1	5	-1	←	←	4	-1	←	126070.933	-2.435	
1	1	5	0	←	←	4	0	←	126008.517	-2.342	
1	1	5	1	←	←	4	1	←	125997.483	-1.935	
1	1	5	2	←	←	4	2	←	126047.814	-2.873	
1	1	5	3	←	←	4	3	←	126075.316	-2.669	
2	1	5	-3	←	←	4	-3	←	125750.415	1.870	
2	1	5	-2	←	←	4	-2	←	125712.513	0.109	
2	1	5	-1	←	←	4	-1	←	125722.800	1.783	
2	1	5	0	←	←	4	0	←	125770.308	1.327	
2	1	5	1	←	←	4	1	←	125802.543	2.263	
2	1	5	2	←	←	4	2	←	125744.843	2.088	
2	1	5	3	←	←	4	3	←	125699.278	0.975	
2	1	5	4	←	←	4	4	←	125724.463	2.962	
0	1	5	0	←	←	4	-1	←	61231.490	3.867	a
0	1	5	1	←	←	4	0	←	226093.183	3.043	
0	1	5	0	←	←	4	1	←	26994.200	-2.245	c
1	1	5	-2	←	←	4	-3	←	93223.750	1.670	
1	1	5	1	←	←	4	0	←	93985.770	-2.275	a
0	1	6	-2	←	←	6	-1	←	270066.054	1.168	
0	1	6	-1	←	←	6	0	←	64612.020	-3.382	a
0	1	6	1	←	←	6	0	←	100164.060	2.517	a
0	1	6	2	←	←	6	1	←	248129.980	0.463	
1	1	6	-3	←	←	6	-2	←	32844.330	-1.101	b
1	1	6	0	←	←	6	1	←	32034.820	-0.536	b
0	1	6	-5	←	←	5	-5	←	151710.019	0.129	
0	1	6	-4	←	←	5	-4	←	151726.480	0.349	
0	1	6	-3	←	←	5	-3	←	151737.906	0.712	
0	1	6	-2	←	←	5	-2	←	151759.756	0.487	

TABLE III—Continued

VTOR	SIGMA	J'	K'	P'	←	J''	K''	P''	FREQUENCY(MHZ)	RESIDUAL(MHZ)	REFERENCE
0	1	6	-1	—	←	5	-1	—	151303.271	0.676	
0	1	6	0	—	←	5	0	—	151654.218	0.485	
0	1	6	1	—	←	5	1	—	152129.003	0.391	
0	1	6	2	—	←	5	2	—	151759.756	0.363	
0	1	6	3	—	←	5	3	—	151733.687	0.359	
0	1	6	4	—	←	5	4	—	151721.656	0.083	
0	1	6	5	—	←	5	5	—	151712.839	0.091	
1	1	6	-4	—	←	5	-4	—	151212.129	0.404	
1	1	6	-3	—	←	5	-3	—	151261.376	-0.564	
1	1	6	-2	—	←	5	-2	—	151244.872	-1.791	
1	1	6	-1	—	←	5	-1	—	151280.419	-2.798	
1	1	6	0	—	←	5	0	—	151196.054	-2.837	
1	1	6	1	—	←	5	1	—	151184.023	-2.325	
1	1	6	2	—	←	5	2	—	151258.007	-3.312	
1	1	6	3	—	←	5	3	—	151284.667	-3.037	
1	1	6	4	—	←	5	4	—	151239.795	-1.770	
1	1	6	5	—	←	5	5	—	151197.949	0.321	
2	1	6	-3	—	←	5	-3	—	150897.216	2.212	
2	1	6	-2	—	←	5	-2	—	150848.339	-0.147	
2	1	6	-1	—	←	5	-1	—	150861.864	2.196	
2	1	6	0	—	←	5	0	—	150922.362	1.746	
2	1	6	1	—	←	5	1	—	150960.115	2.777	
2	1	6	2	—	←	5	2	—	150886.865	2.685	
2	1	6	3	—	←	5	3	—	150833.397	0.987	
2	1	6	4	—	←	5	4	—	150867.724	3.512	
0	1	6	0	—	←	5	-1	—	86690.880	3.687	a
0	1	6	1	—	←	5	0	—	251818.351	3.075	
0	1	6	0	—	←	5	1	—	51964.750	-2.318	a
0	1	6	1	—	←	5	2	—	-96369.980	0.143	a
0	1	7	-2	—	←	7	-1	—	270772.929	0.813	
0	1	7	-1	—	←	7	0	—	64076.190	-3.187	a
0	1	7	1	—	←	7	0	—	100898.580	2.503	a
0	1	7	2	—	←	7	1	—	247566.806	0.628	
1	1	7	-3	—	←	7	-2	—	32874.340	0.408	b
1	1	7	0	—	←	7	1	—	32047.200	-1.155	b
0	1	7	-6	—	←	6	-6	—	176968.115	-0.278	
0	1	7	-5	—	←	6	-5	—	176980.282	0.342	
0	1	7	-4	—	←	6	-4	—	177010.107	0.530	
0	1	7	-3	—	←	6	-3	—	177025.048	0.362	
0	1	7	-2	—	←	6	-2	—	177059.228	0.575	
0	1	7	-1	—	←	6	-1	—	176352.226	0.803	
0	1	7	0	—	←	6	0	—	176888.134	0.685	
0	1	7	1	—	←	6	1	—	177622.509	0.526	
0	1	7	2	—	←	6	2	—	177059.228	0.584	
0	1	7	3	—	←	6	3	—	177021.288	0.407	
0	1	7	5	—	←	6	5	—	176993.700	0.274	
0	1	7	6	—	←	6	6	—	176975.927	0.106	
1	1	7	-6	—	←	6	-6	—	176455.185	-1.521	
1	1	7	-3	—	←	6	-3	—	176470.614	-0.598	
1	1	7	-2	—	←	6	-2	—	176440.898	-1.812	
1	1	7	-1	—	←	6	-1	—	176487.167	-3.256	
1	1	7	0	—	←	6	0	—	176375.859	-3.363	
1	1	7	1	—	←	6	1	—	176363.554	-2.669	
1	1	7	2	—	←	6	2	—	176468.271	-3.941	
1	1	7	3	—	←	6	3	—	176490.888	-3.329	
2	1	7	-3	—	←	6	-3	—	176042.333	2.642	
2	1	7	-2	—	←	6	-2	—	175981.093	0.014	
2	1	7	-1	—	←	6	-1	—	175997.695	2.404	
2	1	7	0	—	←	6	0	—	176072.900	1.829	
2	1	7	1	—	←	6	1	—	176116.142	3.383	
2	1	7	2	—	←	6	2	—	176024.853	3.133	
2	1	7	3	—	←	6	3	—	175964.980	1.491	
0	1	7	-1	—	←	6	-2	—	-93713.900	-0.437	a
0	1	7	1	—	←	6	0	—	277786.620	3.094	
0	1	7	0	—	←	6	1	—	76723.960	-1.945	a

TABLE III—Continued

VTOR	SIGMA	J'	K'	P'	←	J''	K''	P''	FREQUENCY(MHZ)	RESIDUAL(MHZ)	REFERENCE
0	1	7	1	—	←	6	2	—	-70507.410	0.124	a
0	1	8	-2	—	←	8	-1	—	271789.687	0.599	
0	1	8	-1	—	←	8	0	—	63317.500	-3.073	a
0	1	8	1	—	←	8	0	—	101955.370	2.453	a
0	1	8	2	—	←	8	1	—	246769.492	0.762	
1	1	8	-3	—	←	8	-2	—	32922.310	1.819	b
1	1	8	0	—	←	8	1	—	32059.350	-1.707	b
0	1	8	-7	—	←	7	-7	—	202221.923	0.068	
0	1	8	-6	—	←	7	-6	—	202242.685	-0.069	
0	1	8	-5	—	←	7	-5	—	202268.173	0.459	
0	1	8	-4	—	←	7	-4	—	202291.767	0.702	
0	1	8	-3	—	←	7	-3	—	202312.295	1.060	
0	1	8	-2	—	←	7	-2	—	202360.614	0.503	
0	1	8	-1	—	←	7	-1	—	201344.071	0.932	
0	1	8	0	—	←	7	0	—	202102.792	0.849	
0	1	8	1	—	←	7	1	—	203159.521	0.738	
0	1	8	2	—	←	7	2	—	202362.323	0.988	
0	1	8	3	—	←	7	3	—	202308.417	0.602	
0	1	8	4	—	←	7	4	—	202286.777	0.499	
0	1	8	5	—	←	7	5	—	202272.177	0.435	
0	1	8	6	—	←	7	6	—	202251.181	0.290	
0	1	8	7	—	←	7	7	—	202221.923	-0.595	
1	1	8	-3	—	←	7	-3	—	201679.051	-0.902	
1	1	8	-2	—	←	7	-2	—	201631.395	-1.999	
1	1	8	-1	—	←	7	-1	—	201690.819	-3.716	
1	1	8	0	—	←	7	0	—	201546.727	-3.853	
1	1	8	1	—	←	7	1	—	201534.715	-3.163	
1	1	8	2	—	←	7	2	—	201679.051	-4.348	
1	1	8	3	—	←	7	3	—	201693.505	-3.482	
2	1	8	-3	—	←	7	-3	—	201185.350	3.040	
2	1	8	-2	—	←	7	-2	—	201109.813	0.207	
2	1	8	-1	—	←	7	-1	—	201130.223	2.839	
2	1	8	0	—	←	7	0	—	201222.362	2.215	
2	1	8	1	—	←	7	1	—	201269.774	3.503	
2	1	8	2	—	←	7	2	—	201158.495	3.765	
0	1	8	-1	—	←	7	-2	—	-69428.910	0.067	a
0	1	8	0	—	←	7	0	—	304058.666	3.806	
0	1	8	0	—	←	7	1	—	101204.140	-1.726	a
0	1	8	1	—	←	7	2	—	-44407.350	0.045	a
0	1	9	-2	—	←	9	-1	—	273166.757	0.418	
0	1	9	-1	—	←	9	0	—	62308.740	-3.033	a
0	1	9	1	—	←	9	0	—	103389.700	2.378	a
0	1	9	2	—	←	9	1	—	245709.463	1.015	
1	1	9	-3	—	←	9	-2	—	32994.150	3.585	b
1	1	9	0	—	←	9	1	—	32070.150	-2.453	b
0	1	9	-8	—	←	8	-8	—	227468.720	0.170	
0	1	9	-7	—	←	8	-7	—	227490.624	0.188	
0	1	9	-6	—	←	8	-6	—	227514.454	0.074	
0	1	9	-5	—	←	8	-5	—	227543.749	0.964	
0	1	9	-4	—	←	8	-4	—	227571.337	1.023	
0	1	9	-3	—	←	8	-3	—	227597.280	0.575	
0	1	9	-2	—	←	8	-2	—	227663.745	0.695	
0	1	9	-1	—	←	8	-1	—	226286.865	1.066	
0	1	9	0	—	←	8	0	—	227295.629	1.030	
0	1	9	1	—	←	8	1	—	228729.780	0.776	
0	1	9	2	—	←	8	2	—	227669.824	1.102	
0	1	9	3	—	←	8	3	—	227594.789	0.745	
0	1	9	4	—	←	8	4	—	227566.357	0.548	
0	1	9	5	—	←	8	5	—	227548.144	0.671	
0	1	9	6	—	←	8	6	—	227523.730	0.645	
0	1	9	7	—	←	8	7	—	227490.624	-0.251	
0	1	9	8	—	←	8	8	—	227458.544	-0.444	
1	1	9	-3	—	←	8	-3	—	226887.792	-0.266	
1	1	9	-2	—	←	8	-2	—	226816.259	-1.726	
1	1	9	-1	—	←	8	-1	—	226891.747	-3.349	
1	1	9	0	—	←	8	0	—	226707.519	-4.181	

TABLE III—Continued

VTOR	SIGMA	J'	K'	P'	←	J''	K''	P''	FREQUENCY(MHZ)	RESIDUAL(MHZ)	REFERENCE
1	1	9	1	—	←	8	1	—	226696.630	-3.524	
1	1	9	2	—	←	8	2	—	226891.747	-3.159	
1	1	9	3	—	←	8	3	—	226891.747	-3.732	
2	1	9	-3	—	←	8	-3	—	226325.976	3.413	
2	1	9	-2	—	←	8	-2	—	226233.300	-0.186	
2	1	9	-1	—	←	8	-1	—	226258.495	3.051	
2	1	9	0	—	←	8	0	—	226370.019	2.373	
2	1	9	1	—	←	8	1	—	226421.581	3.982	
2	1	9	2	—	←	8	2	—	226286.913	4.349	
2	1	9	3	—	←	8	3	—	226216.454	1.900	
0	1	9	-1	—	←	8	-2	—	-45502.630	0.659	a
0	1	9	1	—	←	8	0	—	330685.399	3.478	
0	1	9	1	—	←	8	2	—	-18039.500	0.226	c
1	1	9	1	—	←	8	0	—	194637.128	-1.969	
0	1	10	-2	—	←	10	-1	—	274941.562	0.108	
0	1	10	-1	—	←	10	0	—	61036.930	-3.060	a
0	1	10	1	—	←	10	0	—	105245.990	2.567	a
0	1	10	2	—	←	10	1	—	244373.027	0.947	
1	1	10	-3	—	←	10	-2	—	33095.660	5.450	b
1	1	10	0	—	←	10	1	—	32078.930	-3.100	b
0	1	10	-9	—	←	9	-9	—	252696.092	-1.219	
0	1	10	-8	—	←	9	-8	—	252731.639	0.890	
0	1	10	-7	—	←	9	-7	—	252756.102	0.315	
0	1	10	-6	—	←	9	-6	—	252783.299	0.371	
0	1	10	-5	—	←	9	-5	—	252816.405	1.276	
0	1	10	-4	—	←	9	-4	—	252848.436	1.395	
0	1	10	-3	—	←	9	-3	—	252882.567	1.605	
0	1	10	-2	—	←	9	-2	—	252967.333	1.109	
0	1	10	-1	—	←	9	-1	—	251192.333	1.224	
0	1	10	0	—	←	9	0	—	252464.159	1.268	
0	1	10	1	—	←	9	1	—	254320.409	1.417	
0	1	10	2	—	←	9	2	—	252984.032	1.407	
0	1	10	3	—	←	9	3	—	252880.399	0.923	
0	1	10	4	—	←	9	4	—	252844.091	0.962	
0	1	10	5	—	←	9	5	—	252821.337	1.041	
0	1	10	6	—	←	9	6	—	252793.212	1.171	
0	1	10	7	—	←	9	7	—	252756.102	0.208	
0	1	10	8	—	←	9	8	—	252720.165	-0.161	
0	1	10	9	—	←	9	9	—	252690.770	0.971	
1	1	10	-3	—	←	9	-3	—	252095.262	-0.150	
1	1	10	-2	—	←	9	-2	—	251993.944	-1.823	
1	1	10	-1	—	←	9	-1	—	252087.987	-3.655	
1	1	10	0	—	←	9	0	—	251856.395	-4.933	
1	1	10	1	—	←	9	1	—	251847.801	-4.100	
1	1	10	2	—	←	9	2	—	252101.171	-5.578	
1	1	10	3	—	←	9	3	—	252085.692	-3.463	
2	1	10	-3	—	←	9	-3	—	251463.866	3.712	
2	1	10	-2	—	←	9	-2	—	251352.001	-0.143	
2	1	10	-1	—	←	9	-1	—	251382.358	3.390	
2	1	10	0	—	←	9	0	—	251515.917	2.551	
2	1	10	1	—	←	9	1	—	251570.507	4.039	
2	1	10	2	—	←	9	2	—	251409.422	4.841	
2	1	10	3	—	←	9	3	—	251335.838	2.302	
0	1	10	0	—	←	9	-1	—	190155.331	4.212	

Lees and Mohammadi (11). If we arbitrarily set d_{ab} to zero in our fit, the determined value of D_{ab} agrees with that of Lees and Mohammadi (11) to within their stated uncertainty.

The quality of our fit to the millimeter spectrum of methyl mercaptan is comparable to the quality of our fit to the analogous spectrum of methanol, which possesses a smaller root-mean-square deviation of 1.18 MHz. However, the 470 lines of methanol fit in our analysis (6) consist of transitions with $J \leq 8$ only. Removal of the $J = 9-10$

TABLE IV
Rotation, Torsion, Distortion, and Interaction Constants of CH₃SH

Constant (MHz unless noted)	Present Value ^a	Other Values ^b
A	102755.3022(3989)	102754. ^c
B	12946.77758(8007)	12942.486 ^c
C	12386.19043(9100)	12389.852 ^c
D _{ab}	-215.70273(9.16922)	-123.4(2.0)
F(cm ⁻¹)	15.069613991(1554354)	15.1082 ^c
ρ(unitless)	0.6522999476(7164)	0.652154 ^c
V ₃ (cm ⁻¹)	443.0289177(699731)	444.763(87)
V ₆ (cm ⁻¹)	-1.6451238(143997)	-2.070(66)
F _v	-61.92878(3783)	-61.744(51)
G _v	-0.9402074(28130)	-0.9245(21)
L _v x 10 ²	-2.55945(49620)	-6.34(33)
D _J x 10 ²	1.58221(1261)	1.59(20)
D _{JK} x 10 ¹	1.050680(4812)	1.062(54)
D _K x 10 ¹	9.042266(821789)	
d _{ab}	114.1845(11.2415)	
k ₁	-46.459260(1.280083)	
δ _J x 10 ³	0.83045(15200)	
δ _K x 10 ¹	-3.17208(40398)	
c ₁	-0.4800796(27639)	
c ₂	-2.50130(9841)	
l _v x 10 ³	-3.97300(59102)	

^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 Reference (11).

^c Taken from combination of constants of reference (11).

transitions of methyl mercaptan results in a reduced root-mean-square deviation of the least-squares fit. In addition, there are a variety of measured and assigned lines of methanol that could not be fit by our IAM treatment. We have not had any comparable difficulties with CH₃SH.

Our least-squares fit to the 612 methyl mercaptan transition frequencies allows us to predict the transition frequencies of over 1900 additional microwave, millimeter, submillimeter, and far-infrared lines of this molecule involving the quantum numbers $J \leq 10$ and $v_t \leq 2$. These transitions all involve no change in the torsional quantum number ($\Delta v_t = 0$). Many of these transition frequencies are predicted to an accuracy of 1–10 MHz and might be of interest to radioastronomers seeking to assign currently unidentified interstellar lines.

Although the IAM treatment utilized is sufficiently accurate to enable us to assign and fit a large number of lines of the methyl mercaptan spectrum, we find that the

treatment, even when subjected to an essentially nonperturbative diagonalization procedure, cannot reproduce the spectrum to its experimental accuracy. One possibility for improving the theoretical treatment is to attempt a one-step diagonalization procedure in which the basis set utilized would be a product of rigid rotor and free internal rotor eigenfunctions rather than the current two-step procedure in which first the torsional Hamiltonian is diagonalized to produce torsional basis functions. Such a procedure would have several advantages including a more rigorous treatment of off-diagonal torsional (or free rotor) matrix elements. However, an analysis based on this procedure would involve the diagonalization of matrices sufficiently large that even for modest maximum cut-off values of J and v_i , a super computer would have to be utilized.

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