The Microwave Spectrum and Quadrupole Coupling Constant Tensor of Bromomethylsilane

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The microwave spectra of four isotopic species of bromomethylsilane have been measured, *viz.*, the ^{79}Br and ^{81}Br species of $BrCH_2SiH_3$ and $BrCH_2SiD_3$. The observed rotational constants have been well explained by a model of which the structural parameters have been transferred from the corresponding parameters determined for ethylbromide and chloromethylsilane. The principal quadrupole coupling constants have been determined through the analysis of the first- and second-order effects of quadrupole coupling on the hyperfine structure of the observed spectra. It was concluded, within the experimental error, that the quadrupole coupling constants tensor of this molecule has the cylindrical symmetry around the largest principal axis, the direction of which coincides approximately with the C–Br internuclear line.

The microwave spectra of ethyl chloride and chloromethylsilane had been investigated by Schwendeman and Jacobs.[1,2] Their works were concerned with the r_s structure, the quadrupole coupling constants and the barrier to the internal rotation of these molecules. Wagner, Dailey, and Solimene[3] had investigated the microwave spectrum of ethyl bromide in relation to the diagonal components of the quadrupole coupling constant tensor referred to the principal inertial axes of the molecule.

Flanagan and Pierce[4] had reinvestigated the microwave spectrum of ethylbromide in order to determine the r_s structure, the barrier to the internal rotation and the quadrupole coupling constant tensor. They had found that in the limit of the first-order quadrupole coupling theory certain transitions show anomalous hyperfine splittings which are removed when the second-order quadrupole coupling effects are considered.

The present work is concerned with the investigation of the microwave spectrum of the ^{79}Br and ^{81}Br species of $BeCH_2SiH_3$ and $BrCH_2SiD_3$.

The approximate molecular structure had been estimated from the observed rotational constants and the quadrupole coupling tensor has been determined from the hyperfine splittings of the spectra. One of our interests on bromomethylsilane was on the barrier height of the internal rotation. Lowe and Parr[5] had estimated the barrier of this molecule to be roughly equal to that for chloromethylsilane (2550 cal/mol) by their semi-empirical theory. However, our preliminary calculations had indicated that the splittings of the spectra due to the internal rotation in the ground and first excited torsional states may be much smaller ($<$0.3 MHz) than the resolving power of our instrument for the transitions with $J<15$ if the barrier is higher than about 2000 cal/mol. As no spectra had actually been observed with the splitting due to the internal rotation, the barrier height cannot be determined at present.

Experimental

The samples of bromomethylsilane and its deuterated species were prepared by the reaction of $SiBr_4$ and diazomethane in ethylether and by the reduction of the resultant $BrCH_2SiBr_3$ with $LiAlH_4$ or $LiAlD_4$ in *n*-butylether.[6]

The microwave spectra of the samples were measured in the region from 8500 to 36000 MHz with conventional sinusoidal and square wave Stark modulation spectrometers at the temperature of dry ice.

Spectra and Analysis

Bromomethylsilane is a slightly asymmetric prolate top molecule with a plane of symmetry perpendicular to the largest moment of inertia. Both "a" and "b" type transitions have been observed. Both ^{79}Br and ^{81}Br have nuclear spin of 3/2, so that for each transition of every species, there are four comparatively intense hyperfine components except for the low J transitions, under the rule of $\Delta F=\Delta J$.

As is shown in Tables 1 and 6, these quartets exhibit more or less asymmetry of the splittings. Since the first-order perturbation theory predicts that for the transitions having $J>3$ the four hyperfine components will appear as two doublets with the equal splitting, the observed asymmetry of the splittings suggests that the perturbation treatment should be extended at least up to the second-order in the analysis of the quadrupole coupling effect.

For the quadrupole coupling tensor in the principal inertial axes system, χ_{ab} is alone the non-zero off-diagonal element from the molecular symmetry. The second-order effects on the hyperfine structure of the spectra, therefore, depend mainly on $|\chi_{ab}|$ when at least one of the energy levels of the transitions is in near degeneracy with the other levels. Since $|\chi_{ab}|$ is estimated to be relatively large, the rotational states within about 30000 MHz can affect with each other beyond the experimental error. Since the second-order perturbation sums relating to χ_{ab} contain the matrix element of $\Phi_{za}\Phi_{zb}$, the sums vanish unless the direct

1) R. H. Schwendeman and G. D. Jacobs, *J. Chem. Phys.*, **36**, 1245 (1962).
2) R. H. Schwendeman and G. D. Jacobs, *ibid.*, **36**, 1251 (1962).
3) R. S. Wagner, B. P. Dailey, and N. Solimene, *ibid.*, **26**, 1593 (1957).
4) C. Flanagan and L. Pierce, *ibid.*, **38**, 2963 (1963).
5) J. P. Lowe and R. G. Parr, *ibid.*, **44**, 3001 (1966).
6) D. Seyferth and E. G. Rochow, *ibid.*, **77**, 907 (1955).

TABLE 1. THE COMPARISON OF THE OBSERVED AND CALCULATED FREQUENCIES OF HYPERFINE COMPONENTS OF BROMOMETHYLSILANE IN MHz

Transition[a]	$^{79}BrCH_2SiH_3$					$^{81}BrCH_2SiH_3$				
		$(\nu-\nu_0)$[b]					$(\nu-\nu_0)$[b]			
	Obsd	Obsd	Calcd	Contribution (1)[c]	Contribution (2)[d]	Obsd	Obsd	Calcd	Contribution (1)[c]	Contribution (2)[d]
$3_{12}\leftarrow3_{03}$	18334.41	19.96	20.55	17.45	3.11	18429.47	16.71	16.60	14.57	2.03
	18380.71	−33.74	−32.74	−34.89	1.93	18384.91	−27.85	−27.83	−29.13	1.30
	18406.54	−7.91	−6.28	−10.47	4.18	18406.54	−6.22	−6.11	−8.74	2.63
	—	—	43.41	41.87	1.54	—	—	36.00	34.96	1.04
$4_{13}\leftarrow4_{04}$	18711.80	13.45	13.33	16.07	−2.74	18704.52	11.54	11.35	13.42	−2.07
	18673.27	−25.08	−25.29	−28.13	2.84	18671.45	−21.53	−21.67	−23.49	1.82
	18681.86	−16.49	−16.34	−12.63	−3.71	18679.31	−13.67	−13.41	−10.55	−2.86
	18734.79	36.44	36.60	31.57	5.03	18722.55	29.57	29.65	26.37	3.28
$5_{14}\leftarrow5_{05}$	19073.05	14.66	14.54	15.54	−1.00	19059.81	12.10	12.25	12.98	−0.72
	19030.73	−27.66	−27.61	−24.86	−2.75	19024.83	−22.88	−22.84	−20.76	−2.08
	19042.87	−15.52	−15.62	−13.47	−2.16	19035.75	−11.96	−12.81	−11.25	−1.57
	19080.99	22.60	22.78	26.93	−4.15	19066.68	18.97	19.36	22.49	−3.13
$6_{15}\leftarrow6_{06}$	19512.01	14.81	14.78	15.40	−0.62	19492.27	12.43	12.41	12.86	−0.45
	19472.99	−24.21	−24.20	−23.10	−1.10	19459.71	−20.13	−20.08	−19.29	−0.79
	19481.81	−15.39	−15.37	−14.00	−1.37	19467.24	−12.60	−12.66	−11.69	−0.97
	19519.93	22.73	22.73	24.50	−1.77	19499.01	19.17	19.19	20.46	−1.26
$7_{16}\leftarrow7_{07}$	20033.14	15.12	15.02	15.48	−0.46	20005.30	12.67	12.60	12.92	−0.32
	19995.14	−22.88	−22.88	−22.11	−0.77	19973.64	−18.99	−19.01	−18.46	−0.55
	20003.77	−14.25	−14.19	−14.46	0.27	19980.84	−11.79	−11.71	−12.07	0.36
	20040.79	22.77	22.79	23.13	−0.34	20011.82	19.19	19.19	19.31	−0.12
$8_{17}\leftarrow8_{08}$	20640.42	15.34	15.34	15.69	−0.35	20602.95	12.92	12.84	13.09	−0.25
	20602.95	−22.13	−22.21	−21.57	−0.64	20571.79	−18.24	−18.46	−18.01	−0.45
	20609.78	−15.30	−15.18	−14.90	−0.28	20577.39	−12.64	−12.63	−12.44	−0.19
	20646.81	21.73	21.70	22.36	−0.65	20608.41	18.38	18.20	18.66	−0.46
$9_{18}\leftarrow9_{09}$	21338.39	15.72	15.70	15.99	−0.29	21289.90	13.20	13.14	13.34	−0.21
	21300.73	−21.94	−21.93	−21.32	−0.61	21258.51	−18.19	−18.22	−17.79	−0.42
	21307.03	−15.64	−15.57	−15.36	−0.21	21263.67	−13.03	−12.98	−12.82	−0.16
	21344.05	21.38	21.34	21.95	−0.61	21294.54	17.84	17.88	18.32	−0.43
$10_{19}\leftarrow10_{010}$	22131.85	15.79	16.11	16.36	−0.25	22070.61	13.48	13.47	13.65	−0.18
	22093.98	−22.08	−21.95	−21.27	−0.68	22038.97	−18.16	−18.21	−17.74	−0.47
	22099.76	−16.30	−16.11	−15.84	−0.26	22043.69	−13.44	−13.40	−13.22	−0.19
	22136.94	20.88	21.02	21.78	−0.77	22074.75	17.62	17.65	18.18	−0.53
$11_{110}\leftarrow11_{011}$	23028.05	17.29	16.56	16.78	−0.22	22950.59	14.00	13.84	14.00	−0.16
	22987.66	−23.10	−22.42	−21.36	−1.06	22918.02	−18.57	−18.50	−17.81	−0.69
	22993.48	−17.28	−16.65	−16.35	−0.30	22922.58	−14.01	−13.84	−13.63	−0.21
	23031.88	21.12	20.51	21.78	−1.27	22953.98	17.39	17.35	18.18	−0.83
$4_{04}\leftarrow3_{03}$	16644.48	−2.73	−2.76	−2.76	0.00	16517.03	−2.32	−2.30	−2.30	0.00
	16642.55	−4.66	−4.51	−2.29	−2.12	16516.00	−3.35	−3.33	−1.92	−1.42
	16653.25	6.04	6.12	7.46	−1.34	16524.71	5.36	5.26	6.22	−0.96
	16650.73	3.52	3.34	6.99	−3.66	16522.80	3.45	3.48	5.83	−2.36
$4_{14}\leftarrow3_{13}$	16369.91	−5.89	−5.88	−5.99	0.11	16246.92	−4.86	−4.92	−4.99	0.08
	16378.38	2.58	2.59	2.61	−0.02	16253.90	2.12	2.16	2.18	−0.01
	16386.34	10.54	10.51	10.54	−0.03	16260.57	8.79	8.78	8.80	−0.02
	—	—	1.81	1.94	−0.14	—	—	1.53	1.63	−0.10
$4_{13}\leftarrow3_{12}$	16921.83	−9.89	−9.98	−4.13	−5.85	16792.27	−7.57	−7.54	−3.44	−4.10
	16934.98	3.26	3.16	4.47	−1.31	16802.63	2.79	2.83	3.73	−0.90
	16927.67	−4.05	−3.94	5.30	−9.24	16797.68	−2.16	−2.04	4.41	−6.45
	16928.17	−3.55	−3.47	−3.30	−0.17	16796.85	−2.99	−2.88	−2.76	−0.12
$5_{05}\leftarrow4_{04}$	20800.79	−2.29	−2.03	−2.03	0.00	20641.42	−1.80	−1.69	−1.69	0.00
	20807.42	4.34	4.43	−1.44	5.87	20646.20	2.98	2.91	−1.21	4.12
	20808.12	5.04	5.13	4.29	0.84	20647.39	4.17	4.15	3.57	0.57
	20814.94	11.86	12.67	3.70	8.96	20652.63	9.41	9.35	3.09	6.26
$5_{15}\leftarrow4_{14}$	20464.36	−3.79	−3.63	−3.85	0.22	20310.08	−3.07	−3.06	−3.21	0.15
	20468.73	0.58	0.65	0.54	0.11	20313.64	0.49	0.53	0.45	0.08
	20474.39	6.24	6.14	6.36	−0.22	20318.30	5.15	5.15	5.31	−0.16
	20470.09	1.94	1.82	1.98	−0.16	20314.76	1.61	1.54	1.65	−0.11

TABLE 1. (Continued)

$5_{14}\leftarrow4_{13}$	21162.11	−1.04	−0.82	−2.56	1.74					
	21165.12	1.97	2.11	1.83	0.28					
	21169.23	6.08	5.85	3.45	2.39					
	21162.11	−1.04	−0.72	−0.94	−0.22					
$6_{06}\leftarrow5_{05}$	24952.65	−1.51	−1.61	−1.61	0.00	24761.56	−1.31	−1.34	−1.34	0.00
	24951.65	−2.51	−2.64	−0.91	−1.73	24760.77	−2.10	−2.10	−0.76	−1.34
	24956.56	2.40	2.48	2.88	−0.40	24765.01	2.14	2.10	2.40	−0.30
	24953.52	−0.64	−0.51	2.18	−2.69	24762.59	−0.28	−0.26	1.82	−2.08
$6_{16}\leftarrow5_{15}$	24556.48	−2.71	−2.65	−2.69	0.04	24371.09	−2.16	−2.22	−2.24	0.03
	24559.07	−0.12	−0.11	−0.09	−0.01	24373.21	−0.04	−0.09	−0.08	−0.01
	24563.31	4.12	4.08	4.19	−0.12	24376.63	3.38	3.42	3.50	−0.08
	24560.69	1.50	1.54	1.60	−0.06	24374.52	1.27	1.30	1.34	−0.04
$6_{15}\leftarrow5_{14}$	25391.72	−1.43	−1.37	−1.75	0.38	25193.99	−1.17	−1.18	−1.46	0.28
	25394.02	0.87	0.77	0.85	−0.08	25195.85	0.69	0.66	0.71	−0.05
	25395.82	2.67	2.74	2.35	0.39	25197.39	2.23	2.25	1.95	0.30
	25392.61	−0.54	−0.57	−0.26	−0.31	25194.72	−0.44	−0.43	−0.22	−0.21
$8_{08}\leftarrow7_{17}$	17122.92	8.56	8.50	8.50	−0.01	16836.45	7.13	7.13	7.13	−0.00
	17100.76	−13.60	−13.61	−14.16	0.55	16817.82	−11.50	−11.47	−11.86	0.39
	17108.01	−6.35	−6.31	−7.35	1.03	16823.79	−5.53	−5.57	−6.16	0.60
	17131.09	16.73	16.75	15.31	1.44	16843.05	13.73	13.75	12.83	0.92
$9_{09}\leftarrow8_{18}$	21761.49	8.97	8.94	8.95	−0.01	21437.00	7.38	7.50	7.50	−0.00
	21739.01	−13.51	−13.43	−13.91	0.48	21418.32	−11.30	−11.32	−11.66	0.34
	21744.02	−8.50	−8.48	−8.08	−0.40	21422.58	−7.04	−7.07	−6.78	−0.29
	21767.67	15.15	15.06	14.77	0.29	21442.25	12.63	12.58	12.38	0.20
$10_{010}\leftarrow9_{19}$	26440.09	9.16	9.14	9.15	−0.01	26077.84	7.67	7.67	7.68	−0.00
	26417.84	−13.09	−13.06	−13.52	0.98	26059.19	−10.98	−11.01	−11.34	0.32
	26422.30	−8.63	−8.62	−8.49	−0.13	26062.99	−7.18	−7.22	−7.12	−0.10
	26445.53	14.60	14.63	14.18	0.45	26082.31	12.14	12.20	11.89	0.31

Transition[a]	$^{79}BrCH_2SiD_3$					$^{81}BrCH_2SiD_3$				
				$(\nu-\nu_0)$[b]					$(\nu-\nu_0)$[b]	
					Contribution					Contribution
	Obsd	Obsd	Calcd	(1)[c]	(2)[d]	Obsd	Obsd	Calcd	(1)[c]	(2)[d]
$4_{13}\leftarrow4_{04}$	15126.24	14.68	14.80	16.41	−1.61	15123.00	12.28	12.50	13.66	−1.16
	15066.55	−45.01	−45.66	−28.72	−16.94	15069.32	−41.40	−41.62	−23.91	−17.71
	—	—	−20.14	−12.90	−7.24	—	—	−17.38	−10.74	−6.65
	15116.68	5.12	4.87	32.24	−27.37	15109.51	−1.21	−1.82	26.84	−28.66
$5_{14}\leftarrow5_{05}$	15421.53	15.09	15.07	15.94	−0.87	15413.79	12.70	12.66	13.27	−0.62
	15379.32	−27.12	−27.25	−25.51	−1.74	15378.64	−22.45	−22.49	−21.24	−1.25
	15390.88	−15.56	−15.74	−13.82	−1.93	15388.16	−12.93	−12.87	−11.50	−1.36
	15431.52	25.08	24.89	27.63	−2.74	15422.16	21.07	21.04	23.01	−1.97
$6_{15}\leftarrow6_{06}$	15781.36	15.27	15.25	15.85	−0.60	15767.70	12.58	12.77	13.20	−0.42
	15741.12	−24.97	−24.80	−23.78	−1.02	15734.56	−20.56	−20.52	−19.80	−0.73
	15746.79	−19.30	−19.26	−14.41	−4.85	15741.12	−14.00	−14.25	−12.00	−2.25
	15787.63	21.54	21.15	25.22	−4.07	15774.11	18.99	18.93	21.00	−2.07
$7_{16}\leftarrow7_{07}$	16208.53	15.53	15.51	15.97	−0.46	16188.14	12.97	12.97	13.30	−0.33
	16169.51	−23.49	−23.62	−22.81	−0.81	16155.66	−19.51	−19.56	−18.99	−0.57
	16177.64	−15.36	−15.28	−14.92	−0.37	16162.46	−12.71	−12.67	−12.42	−0.25
	16216.01	23.01	23.03	23.87	−0.84	16194.48	19.31	19.29	19.87	−0.58
$8_{17}\leftarrow8_{08}$	16706.60	15.84	15.84	16.22	−0.38	16678.09	13.23	13.23	13.50	−0.22
	16667.80	−22.96	−23.07	−23.30	−0.77	16645.71	−19.15	−19.10	−18.56	−0.54
	16675.06	−15.70	−15.69	−15.41	−0.28	16651.85	−13.01	−13.04	−12.82	−0.21
	16713.03	22.27	22.31	23.11	−0.80	16683.60	18.74	18.67	19.24	−0.56
$9_{18}\leftarrow9_{09}$	17279.11	16.17	16.24	16.55	−0.31	17241.21	13.53	13.56	13.78	−0.22
	17240.09	−22.85	−22.96	−22.07	−0.89	17208.83	−18.85	−18.97	−18.37	−0.60
	17246.69	−16.25	−16.24	−15.90	−0.34	17214.20	−13.48	−13.47	−13.24	−0.24
	17284.64	21.70	21.69	22.72	−1.03	17245.82	18.14	18.21	18.91	−0.70
$10_{19}\leftarrow10_{010}$	17930.44	16.68	16.68	16.95	−0.27	17881.53	13.90	13.92	14.11	−0.19
	17890.16	−23.60	−23.73	−22.04	−1.69	17848.26	−19.37	−19.40	−18.34	−1.06

TABLE 1. (Continued)

	17896.94	−16.82	−16.81	−16.42	−0.39	17853.73	−13.90	−13.93	−13.66	−0.27
	17934.25	20.49	20.51	22.58	−2.06	17885.11	17.48	17.49	18.78	−1.29
11_{110}←11_{011}	18664.89	17.06	17.16	17.41	−0.24	18603.36	14.11	14.31	14.48	−0.17
	18627.66	−20.17	−20.24	−22.15	1.91	18572.80	−16.45	−16.64	−18.43	1.79
	18630.46	−17.37	−17.19	−16.95	−0.24	18574.96	−14.29	−14.30	−14.10	−0.16
	18672.87	25.04	24.90	22.61	2.29	18610.20	20.95	20.95	18.80	2.15
4_{04}←3_{03}	15239.76	−2.61	−2.71	−2.71	0.00	15118.74	−2.09	−2.25	−2.25	0.00
	15257.33	14.96	16.25	−2.22	18.47	—	—	16.90	−1.85	18.74
	15254.05	11.68	11.98	7.31	4.67	15131.39	10.56	10.82	6.06	4.75
	15279.93	37.56	37.11	6.82	30.29	—	—	36.28	5.66	30.62
4_{14}←3_{13}	15013.37	−6.21	−5.80	−5.91	0.11					
	15021.57	1.99	2.38	2.51	−0.13					
	15030.44	10.86	10.40	10.47	−0.07					
	15021.57	1.99	1.73	2.05	−0.33					
4_{13}←3_{12}						15359.31	9.23	13.11	−3.30	16.41
						15358.15	8.07	7.94	3.68	4.26
						15383.43	33.35	30.84	4.16	26.68
						15347.59	−2.49	−3.08	−2.83	−0.25
5_{05}←4_{04}	19044.65	−2.38	−2.00	−2.00	0.00	18894.62	−2.49	−1.66	−1.66	0.00
	19033.63	−13.40	−16.49	−1.39	−15.11	18881.03	−16.08	−17.55	−1.15	−16.39
	19046.89	−0.14	−0.26	4.31	−4.48	18895.57	−1.54	−1.16	3.49	−4.65
	19023.57	−23.46	−21.33	3.59	−24.93	—	—	−23.92	2.99	−26.90
5_{15}←4_{14}	18768.83	−3.65	−3.57	−3.80	0.24	18623.04	−3.11	−2.99	−3.16	0.17
	18772.99	0.51	0.59	0.50	0.10	18626.53	0.38	0.48	0.41	0.07
	18778.54	6.06	6.03	6.32	−0.28	18631.30	5.15	5.05	5.25	−0.19
	18774.37	1.89	1.81	2.02	−0.21	18627.80	1.65	1.53	1.68	−0.14
5_{14}←4_{13}	19340.03	−1.67	−1.73	−2.47	0.75	19185.46	−1.61	−1.50	−2.05	0.55
	19343.71	2.01	1.92	1.83	0.08	19188.64	1.57	1.59	1.52	0.07
	19345.97	4.27	4.13	3.29	0.84	19190.58	3.51	3.36	2.72	0.63
	19340.03	−1.67	−1.31	−1.10	−0.30	19185.95	−1.12	−1.05	−0.85	−0.21
6_{06}←5_{05}	22846.83	−1.56	−1.60	−1.60	0.00	22666.98	−1.25	−1.32	−1.32	0.00
	22846.83	−1.56	−1.59	−0.86	−0.73	22666.98	−1.25	−1.25	−0.72	−0.54
	22850.91	2.52	2.60	2.84	−0.23	22670.38	2.15	2.18	2.35	−0.17
	22849.31	0.92	0.90	2.10	−1.20	22669.13	0.90	0.87	1.74	−0.88
6_{16}←5_{15}	22522.29	−2.73	−2.65	−2.66	0.01	22347.25	−2.17	−2.20	−2.21	0.01
	22524.91	−0.11	−0.15	−0.11	−0.04	22349.33	−0.09	−0.13	−0.10	−0.03
	22528.67	3.65	3.56	4.16	−0.60	22352.50	3.08	3.09	3.46	−0.37
	22526.23	1.21	1.28	1.61	−0.34	22350.49	1.07	1.14	1.34	−0.21
6_{15}←5_{14}	23206.52	−1.41	−1.42	−1.69	0.27	23021.05	−1.18	−1.21	−1.40	0.19
	23208.81	0.88	0.86	0.87	−0.01	23022.95	0.72	0.72	0.72	−0.01
	23206.68	−1.25	−0.91	2.24	−3.15	23022.95	0.72	0.81	1.86	−1.05
	23205.39	−2.54	−2.85	−0.32	−2.53	23021.05	−1.18	−1.25	−0.27	−0.98
7_{07}←6_{16}	13278.84	8.19	8.22	8.20	0.02	13043.14	6.91	6.88	6.87	0.02
	13256.58	−14.07	−14.12	−14.84	0.71	13024.39	−11.84	−11.90	−12.40	0.50
	13264.77	−5.88	−5.86	−6.57	0.70	13031.10	−5.13	−5.06	−5.50	0.44
	13288.45	17.80	17.85	16.47	1.38	13050.88	14.65	14.70	13.76	0.94
8_{08}←7_{17}	17442.08	8.93	8.96	8.97	−0.01	17171.53	7.53	7.50	7.51	−0.01
	17418.91	−14.24	−14.18	−14.78	0.60	17152.10	−11.90	−11.94	−12.36	0.42
	17424.80	−8.35	−8.32	−7.79	−0.53	17157.05	−6.95	−6.91	−6.53	−0.39
	17449.55	16.40	16.33	15.96	0.37	17177.55	13.55	13.59	13.34	0.25
9_{09}←8_{18}	21642.25	9.40	9.38	9.39	−0.01	21336.62	7.83	7.86	7.86	−0.01
	21618.86	−13.99	−13.92	−14.49	0.57	21317.07	−11.72	−11.72	−12.12	0.40
	21624.13	−8.72	−8.67	−8.51	−0.16	21321.58	−7.21	−7.24	−7.13	−0.11
	21648.85	16.00	15.95	15.37	0.58	21342.02	13.23	13.25	12.85	0.40

a) The frequencies of the hyperfine components of the transitions are shown in the order of F'←F=(J'+3/2←J+3/2), (J'+1/2←J+1/2), (J'−1/2←J−1/2), (J'−3/2←J−3/2) where J' and J indicate the rotational quantum number of the higher and lower energy levels of the transition, respectively. The dash indicates that the component of the quartet is actually either completely obscured by the other spectra or defectively resolved from the other spectra.

b) The frequency difference of the hyperfine component (ν) and the hypothetical unsplit frequency (ν_0) of the transition.

c) The contribution to $\nu-\nu_0$ from the first-order theory.

d) The contribution to $\nu-\nu_0$ from the second-order theory.

Table 2. Hypothetical unsplit frequencies (ν_0) of bromomethylsilane in MHz

Transition	$^{79}BrCH_2SiH_3$		$^{81}BrCH_2SiH_3$		$^{79}BrCH_2SiHD_3$		$^{81}BrCH_2SiD_3$	
$3_{12}\leftarrow 3_{03}$	18414.45	(0.32)[a]	18412.76	(−0.15)				
$4_{13}\leftarrow 4_{04}$	18698.35	(−0.21)	18692.98	(−0.16)	15111.56	(0.05)	15110.72	(0.06)
$5_{14}\leftarrow 5_{05}$	19058.39	(−0.23)	19047.71	(−0.08)	15406.44	(−0.11)	15401.09	(−0.07)
$6_{15}\leftarrow 6_{06}$	19497.20	(−0.06)	19479.84	(0.07)	15766.09	(0.04)	15755.12	(0.09)
$7_{16}\leftarrow 7_{07}$	20018.02	(−0.00)	19992.63	(0.14)	16193.00	(0.04)	16175.17	(0.01)
$8_{17}\leftarrow 8_{08}$	20625.08	(0.10)	20590.03	(0.10)	16690.76	(0.11)	16664.86	(0.05)
$9_{18}\leftarrow 9_{09}$	21322.67	(−0.02)	21276.70	(0.19)	17262.94	(0.04)	17227.68	(0.02)
$10_{19}\leftarrow 10_{010}$	22116.06	(−0.07)	22057.13	(0.06)	17913.76	(−0.07)	17867.63	(−0.07)
$11_{110}\leftarrow 11_{011}$	23010.76	(0.11)	22936.59	(−0.24)	18647.83	(−0.07)	18589.25	(−0.02)
$4_{04}\leftarrow 3_{03}$	16647.21	(−0.25)	16519.35	(−0.24)	15242.37	(0.71)	15120.83	(−0.33)
$4_{14}\leftarrow 3_{13}$	16375.80	(−0.10)	16251.78	(−0.09)	15019.56	(0.25)		
$4_{13}\leftarrow 3_{12}$	16931.72	(−0.17)	16799.84	(0.03)			15350.08	(−0.56)
$5_{05}\leftarrow 4_{04}$	20803.08	(0.10)	20643.22	(−0.09)	19047.03	(0.17)	18897.11	(0.72)
$5_{15}\leftarrow 4_{14}$	20468.15	(0.07)	20313.15	(0.07)	18772.48	(−0.23)	18626.15	(−0.01)
$5_{14}\leftarrow 4_{13}$	21163.15	(0.11)			19341.70	(−0.19)	19187.07	(0.20)
$6_{06}\leftarrow 5_{05}$	24954.16	(−0.12)	24762.87	(−0.07)	22848.39	(−0.18)	22668.23	(−0.04)
$6_{16}\leftarrow 5_{15}$	24559.19	(0.12)	24373.25	(0.12)	22525.02	(−0.11)	22349.42	(0.05)
$6_{15}\leftarrow 5_{14}$	25393.15	(0.23)	25195.16	(0.25)	23207.93	(0.28)	23022.23	(−0.01)
$7_{07}\leftarrow 6_{16}$					13270.65	(−0.00)	13036.23	(0.12)
$8_{08}\leftarrow 7_{17}$	17114.36	(−0.04)	16829.32	(0.00)	17433.15	(0.04)	17164.00	(0.04)
$9_{09}\leftarrow 8_{18}$	21752.52	(−0.01)	21429.62	(−0.07)	21632.85	(−0.01)	21328.79	(−0.09)
$10_{010}\leftarrow 9_{19}$	26430.93	(−0.02)	26070.17	(0.00)				

a) Obsd−Calcd

Table 3. Rotational constants (MHz) and moments of inertia[a] (amu·Å^2) for bromomethylsilane

	$^{79}BrCH_2SiH_3$		$^{81}BrCH_2SiH_3$		$^{79}BrCH_2SiD_3$		$^{81}BrCH_2SiD_3$	
	Obsd	Uncertainty[b]	Obsd	Uncertainty[b]	Obsd	Uncertainty[b]	Obsd	Uncertainty[b]
A	20075.59	0.49	20064.50	0.43	16440.09	0.45	16432.87	0.34
B	2151.50	0.02	2134.48	0.02	1963.01	0.02	1947.07	0.02
C	2012.49	0.03	1997.49	0.02	1849.16	0.02	1834.91	0.02
D_J[c]	0.0017	0.0003	0.0017	0.0003	0.0012	0.0004	0.0010	0.0003
	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd
I_a	25.1814	25.1896	25.1953	25.2030	30.7499	30.7462	30.7634	30.7591
I_b	234.9668	236.1919	236.8404	238.0784	257.5285	258.9107	259.6368	261.0310
I_c	251.1968	252.1968	253.0831	254.0957	273.3841	274.4483	275.5072	276.5805
$I_a+I_b-I_c$	8.9514	9.1847	8.9525	9.1857	14.8943	15.2087	14.8929	15.2097

a) Conversion factor; 505531 MHz·amu·Å^2.
b) The uncertainty is calculated only from 2.5 times the standard deviation of the hypothetical unsplit frequencies to fit in with the modified rigid rotor expression.
c) The coefficient of the $[J(J+1)]^2$ term, see the text.

Table 4. The comparison of structural parameters

	$BrCH_2SiH_3$[a]	$ClCH_2SiH_3$[b]		$BrCH_2CH_3$[c]	$ClCH_2CH_3$[d]
r(SiC) (Å)	1.889	1.889	r(CC) (Å)	1.518	1.520
r(CX) (Å)	1.950	1.788	r(CX) (Å)	1.950	1.788
r(CH) (Å)	1.096	1.096	r(CH)CH_2 (Å)	1.087	1.089
r(SiH) (Å)	1.477	1.477	r(CH)CH_3 (Å)	1.093	1.091
α(SiCX)	109°18′	109°18′	α(CCX)	111°2′	111°2′
α(HSiH)	110°36′	110°36′	α(HCH)CH_3	108°52′	108°31′
α(HCH)	107°30′	107°30′	α(HCH)CH_2	109°54′	109°12′
α(SiCH)	109°18′	109°18′	α(CH_3CH)	105°25′	106°35′

a) This work, b) Footnote 2, c) Footnote 4, d) Footnote 1.

TABLE 5. QUADRUPOLE COUPLING CONSTANTS[a)]

		$^{79}BrCH_2SiH_3$		$^{81}BrCH_2SiH_3$		$^{79}BrCH_2SiD_3$		$^{81}BrCH_2SiD_3$	
χ_{aa}	(MHz)	339.6	(10.6)	283.2	(8.0)	332.0	(17.6)	275.5	(13.3)
$\eta\chi_{aa}$[b)]	(MHz)	244.8	(2.4)	204.6	(1.7)	254.1	(3.1)	211.9	(2.2)
χ_{ab}	(MHz)	381.4	(10.6)	319.1	(10.1)	399.1	(11.1)	332.6	(13.7)
χ_{zz}	(MHz)	573.7	(1.1)	479.5	(2.8)	586.6	(3.9)	488.3	(1.9)
χ_{xx}	(MHz)	−281.6	(18.3)	−235.6	(15.6)	−293.5	(31.8)	−244.6	(23.0)
χ_{yy}	(MHz)	−292.2	(6.5)	−243.9	(4.8)	−293.1	(10.3)	−243.7	(7.8)
η_{bond}[c)]		0.0185	(0.043)	0.0174	(0.043)	−0.0008	(0.072)	−0.0017	(0.063)
θ_{za}[d)]		31°33′	(40′)	31°36′	(41′)	32°32′	(1°5′)	32°36′	(56′)
θ[e)]		31°57′		31°55′		32°33′		32°30′	
$\chi_{zz}^{79}/\chi_{zz}^{81}$[f)]		1.1965				1.2014			

a) a, b, and c designate the principal intertial axes and z, x, and y designate the principal axes of the χ tensor. The figure in the parentheses indicates the uncertainty calculated from the standard deviation of the splittings.
b) $\eta=(\chi_{bb}-\chi_{cc})/\chi_{aa}$
c) $\eta_{bond}=(\chi_{xx}-\chi_{yy})/\chi_{zz}$
d) θ_{za} is the angle between the "a" inertial axis of the molecule and the "z" principal axis of the χ tensor.
e) θ is the angle between the "a" inertial axis and the C–Br internuclear line.
f) The reported ratio of the quadrupole moments of ^{79}Br and ^{81}Br is 1.19707.

TABLE 6. THE OBSERVED AND CALCULATED ASYMMETRY OF THE SPLITTINGS IN MHz[a)]

Transition	$^{79}BrCH_2SiH_3$			$^{81}BrCH_2SiH_3$			$^{79}BrCH_2SiD_3$			$^{81}BrCH_2SiD_3$		
	Obsd	Calcd total	Calcd one level[b)]	Obsd	Calcd total	Calcd one level[b)]	Obsd	Calcd total	Calcd one level[b)]	Obsd	Calcd total	Calcd one level[b)]
$3_{12}\leftarrow3_{03}$	−2.38[c)]	−3.82	−5.38	−2.19[c)]	−2.31	−3.57						
$4_{13}\leftarrow4_{04}$	14.40	14.32	13.96	10.17	10.03	10.12	−37.27[c)]	−35.45	−30.72	−42.71[c)]	−38.57	−32.60
$5_{14}\leftarrow5_{05}$	−4.20	−3.74	−4.13	−4.05	−2.92	−3.31	−1.57	−1.68	−1.50	−1.15	−1.24	−1.08
$6_{15}\leftarrow6_{06}$	−0.90	−0.87	−0.89	−0.79	−0.64	−0.68	0.60	0.35	−0.54	−0.15	−0.14	0.38
$7_{16}\leftarrow7_{07}$	−0.93	−0.92	−0.39	−0.68	−0.70	−0.29	−0.65	−0.82	−0.28	−0.46	−0.57	−0.19
$8_{17}\leftarrow8_{08}$	−0.44	−0.66	−0.22	−0.14	−0.46	−0.16	−0.83	−0.94	−0.17	−0.63	−0.62	−0.12
$9_{18}\leftarrow9_{09}$	−0.64	−0.70	−0.14	−0.52	−0.49	−0.10	−1.07	−1.27	−0.11	−0.76	−0.84	−0.08
$10_{19}\leftarrow10_{010}$	−0.69	−0.93	−0.10	−0.58	−0.63	−0.07	−2.97	−3.09	−0.08	−1.89	−1.89	−0.06
$11_{110}\leftarrow11_{011}$	−1.99	−1.80	−0.07	−1.17	−1.15	−0.05	5.18	4.69	−0.06	4.68	4.26	−0.04
$4_{04}\leftarrow3_{03}$	−4.45	−4.53	−5.38	−2.94	−2.96	−3.57	43.45	44.09	37.38	—	44.61	37.14
$4_{14}\leftarrow3_{13}$	−0.18[c)]	−0.23	0.00	−0.11[c)]	−0.16	0.00	−0.67	−0.49	0.00			
$4_{13}\leftarrow3_{12}$	13.65	13.62	13.96	9.53	9.53	10.12				−37.00	−39.09	−32.60
$5_{05}\leftarrow4_{04}$	13.45	13.99	13.96	10.02	9.80	10.12	−34.34	−35.56	−30.72	−36.29[c)]	−38.65	−32.60
$5_{15}\leftarrow4_{14}$	0.07	−0.04	0.00	0.02	−0.03	0.00	−0.01	−0.07	0.00	−0.01	−0.05	0.00
$5_{14}\leftarrow4_{13}$	−4.11	−4.07	−4.13				−1.45	−1.80	−1.50	−1.45	−1.32	−1.08
$6_{06}\leftarrow5_{05}$	−4.04	−4.03	−4.13	−3.21	−3.12	−3.31	−1.25	−1.70	−1.50	−1.25	−1.25	−1.08
$6_{16}\leftarrow5_{15}$	−0.03	0.00	0.00	0.01	−0.00	0.00	0.18	0.21	0.00	0.07	0.13	0.00
$6_{15}\leftarrow5_{14}$	−0.91	−1.16	−0.89	−0.81	−0.84	−0.68	0.90	0.34	−0.54	0.00	−0.13	−0.38
$7_{07}\leftarrow6_{16}$							1.03	1.37	1.14	1.03	0.98	0.79
$8_{08}\leftarrow7_{17}$	0.92	0.97	1.01	0.63	0.72	0.75	1.58	1.52	0.87	1.07	1.07	0.60
$9_{09}\leftarrow8_{18}$	1.17	1.17	0.79	0.99	0.82	0.59	1.33	1.32	0.70	0.89	0.92	0.48
$10_{010}\leftarrow9_{19}$	0.98	1.04	0.66	0.67	0.73	0.48						

a) The definition of the asymmetry of the splittings is in Eq. (1) in the text.
b) The contribution of $\delta\nu$ from a pair of levels in near degeneracy using the formula given in Eq. (2) in the text.
c) For these transitions, since one of the components of the quartets is obscured by the other spectra, the calculated frequency is used instead of the observed one for this component.

product of the representation of the two rotational states is equal to that of $\Phi_{za}\Phi_{zb}$. Then, the direct product of the representations of the states which are able to couple with each other should be belonging to the B_c species of the four group. Therefore, the number of the rotational states having the second-order quadrupole effects is much restricted.

Since the molecule is too close to the symmetric top, the transitions having $K_{-1}>1$ become to be weak and furthermore, the K degeneracy makes the hyperfine structure analysis of the observed spectra too complicated. Therefore, the measurements were not extended to these transitions. From the observed quartets, the analysis was performed by the following procedures.

First, rough values of the rotational constants were determined by fitting the averaged frequencies of the components for each quartet to the rigid rotor expression.

Second, the asymmetry of the splitting was defined for each quartet as:

$$\delta\nu = \nu(J'+1/2\leftarrow J+1/2) + \nu(J'-3/2\leftarrow J-3/2) - \nu(J'+3/2\leftarrow J+3/2) - \nu(J'-1/2\leftarrow J-1/2) \quad (1)$$
$$= a\chi_{ab}^2 + b\chi_{aa}^2 + c\eta\chi_{aa}^2 + d\eta^2\chi_{aa}^2$$

where $\nu(J'+1/2\leftarrow J+1/2)$ indicates a component of a quartet having $F'=J'+1/2$ and $F=J+1/2$ for the higher and lower levels of the transition, respectively, and so on, and a, b, c, and d are the constants depending on the structure and the type of the transition.

Then, χ_{ab} was obtained taking average of the χ_{ab} values derived from the observed $\delta\nu$ for each quartet.

Third, the observed quartets were corrected by subtracting the contributions of the χ_{ab} terms and the hypothetical quartet patterns due to the first-order quadrupole coupling effects were obtained from which the values of χ_{aa} and $\eta(=(\chi_{bb}-\chi_{cc})/\chi_{aa})$ were determined by the least-squares technique.

Fourth, the unperturbed frequencies for the transitions were calculated by fitting the calculated frequencies of the components of the quartets including both the first- and second-order contributions with the observed.

Fifth, by the least-squares technique the rotational constants were recalculated by fitting the obtained unperturbed frequencies to the rigid rotor expression modified by the term of $-D_J[J(J+1)]^2$ of the centrifugal distortion.

The procedures were repeated until the self-consistent results were obtained. For some of the transitions small χ_{aa}^2, $\eta\chi_{aa}^2$, and $\eta^2\chi_{aa}^2$ contributions were also included in the second-order perturbation corrections. The results are shown in Tables 1, 2, 3, and 5.

Discussion

Structure. Since the observed rotational constants of a sufficient number of the isotopic species are not available, the r_s structure of the molecule cannot be obtained at present. However, when the structural parameters for this molecule are assumed to be equal to those of chloromethylsilane except r(C–Br) which is taken to be equal to that of ethylbromide, the calculated moments of inertia reproduce the observed ones within the deviation of 0.6%.

As is shown in Table 4, the structural parameters of the skeleton of ethyl chloride and bromide are found to be essentially identical except r(C–Br), while r(C–Cl) is found to be identical for ethyl chloride and chloromethylsilane. Then, it is not surprising that the above set of the structural parameters for bromomethylsilane gives an excellent agreement between the calculated and the observed moments of inertia. Therefore, this structure may be proposed as the best structure of bromomethylsilane at present.

Quadrupole Coupling Tensor. As both diagonal and off-diagonal elements of the χ tensor in the inertial principal axis system are obtained, the own principal values and the own principal axis system of the χ tensor can easily be evaluated by diagonalization. As is shown in Table 5 the asymmetry parameter η_{bond} $(=(\chi_{xx}-\chi_{yy})/\chi_{zz})$ around the axis of the largest principal value χ_{zz} is close to zero so that the charge distribution is approximately axially symmetric about the z axis within the limit of the experimental error for all of the isotopic species. The angle θ_{za} which is the angle between the z axis and the "a" inertial principal axis, is also shown and compared with the angle θ which is the angle between the C–Br internuclear line and the "a" axis calculated from the structure mentioned above. The discrepancies between θ_{za} and θ are within about 30′ and the two angles can be regarded as essentially identical.

Then, it can be concluded that the C–Br bond in this molecule seems not to be bent within the limit of the experimental error.

The magnitude of the largest principal quadrupole coupling constant χ_{zz} can be related to the ionic character of the bond.

If the d and the double-bond characters of the bond orbital are neglected, the ionic character i is found by the equation:

$$i = (1-s^2) - (\chi_{zz}/\chi_{at})$$

where s is the s character of the bond orbital and may be taken to be $s^2=0.15$. $\chi_{at}=eQq_{at}$ is the quadrupole coupling constant of the atom and is taken to be $+769.76$ MHz[7] for ^{79}Br. Then, the ionicity of the C–Br bond in bromomethylsilane is calculated to be 10%, while that for ethyl bromide is calculated to be 14%.

The ratio of the quadrupole moments between ^{79}Br and ^{81}Br are found to be 1.1965 and 1.2014 for $BrCH_2SiH_3$ and $BrCH_2SiD_3$, respectively, which give an excellent agreement with the reported value (1.19707).[8]

Asymmetry of the Splittings. As already was mentioned, the asymmetry of the splittings has been removed when the second-order quadrupole coupling effects are considered. Since bromomethylsilane is so nearly a symmetric top, the calculation of the second-order quadrupole effects can be much simplified. Furthermore, near degeneracy of the energy levels occurs usually only in a pair of the levels having relatively low J and $K_{-1}=0$ or 1, that is, the levels $J_{1,J-1}$ and J_{0J} are in near degeneracy with $(J+1)_{0,J+1}$ and $(J-1)_{1,J-2}$, respectively.

Therefore, the asymmetry of the splittings $\delta\nu$ defined in Eq. (1) for these low transitions can be approximately expressed as the following formula without a serious error in comparison with the experimental error.

$$\begin{aligned}
&\delta\nu = [\delta\nu_1(J)-\delta\nu_2(J)]\chi_{ab}^2 && \text{for } J_{1,J-1}\leftarrow J_{0J}\\
&\delta\nu = [\delta\nu_2(J)-\delta\nu_2(J-1)]\chi_{ab}^2 && \text{for } J_{0J}\leftarrow(J-1)_{0,J-1}\\
&\delta\nu = 0 && \text{for } J_{1J}\leftarrow(J-1)_{1,J-1}\\
&\delta\nu = [\delta\nu_1(J)-\delta\nu_1(J-1)]\chi_{ab}^2 && \text{for } J_{1,J-1}\leftarrow(J-1)_{1,J-2}\\
&\delta\nu = [\delta\nu_2(J)]\chi_{ab}^2 && \text{for } J_{0J}\leftarrow(J-1)_{1,J-1}
\end{aligned} \quad (2)$$

where

$$\delta\nu_1(J) = \left[\frac{12(J+2)-J^2(2J+1)(2J+5)-(J+2)^2(2J-1)(2J+3)}{24J(J+1)(2J+1)(2J+3)\Delta E_1(J)}\right] \quad (3)$$

$$\Delta E_1(J) = \left[A-\frac{1}{2}(B+C)\right]\left[1+\frac{J(J+1)}{2}b_p\right] - 2(J+1)\left(\frac{B+C}{2}\right) \quad (4)$$

7) T. M. Sugden and C. N. Kenney, "Microwave Spectroscopy of Gases," Van Nostrand Co., London (1965), p. 121.

8) C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy," McGraw-Hill Book Co., New York (1955), p. 645.

and $\delta\nu_2$ can be obtained by replacing J with $J-1$ and $\Delta E_2(J)=-\Delta E_1(J-1)$. As is shown in Table 6, the calculated $\delta\nu$ by the formula (2) which is labeled as "one level", gives a large portion of the total $\delta\nu$ of the transitions with $J<6$ for every isotopic species so that we may neglect the other contributions. However, the contribution becomes smaller as J increases except $J_{0J}\leftarrow(J-1)_{1,J-1}$ where this is still large even for the transitions with $J>6$.

Since the dependence on the molecular asymmetry is completely neglected for the matrix elements of $\Phi_{za}\Phi_{zb}$ on the derivation of Eq. (2), the above formula will be invalid if the molecular asymmetry increases. However, we believe, these will be useful for the molecules having Ray's asymmetry parameter $|\kappa|>0.90$.