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The Microwave Spectra, Molecular Structures, and Quadrupole Coupling Constants of Methyltrichlorosilane and Trichlorosilane

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Synopsis. The microwave spectrum of methyltrichlorosilane has been re-examined in order to determine the precise molecular structure by observing the spectra due to the isotopic species. The previously reported value of the nuclear quadrupole coupling constant of trichlorosilane has been corrected by the reinvestigation of the hyperfine structure.

The microwave spectra of methyltrichlorosilane and its isotopic species have been investigated first by Mockler *et al.*[1] and recently by Mitzlaff *et al.*[2] In both cases, the spectrum arising from the silicon isotopic species has not been observed, and therefore the precise molecular structure has not been determined. We reinvestigated the microwave spectrum of this molecule in order to obtain the spectrum of the silicon isotopic species, and succeeded in observing it. Furthermore, we found the spectrum of the ^{13}C species at frequencies different from the previously reported values. In their paper[2] Mitzlaff *et al.* have also reported the quadrupole coupling constant of trichlorosilane. Their value, however, seemed too small compared with that of chlorosilane. We reinvestigated the spectrum of this molecule and corrected their value. In this paper we report the newly determined molecular constants and the precise molecular structures of methyltrichlorosilane and trichlorosilane.

Methyltrichlorosilane. The spectra were examined with a conventional 100 kHz Stark-modulation spectrometer, with a 3-m X-band waveguide cell. Both ^{29}Si and ^{13}C species were measured in natural abundances. To obtain the spectrum due to the ^{29}Si species, the regions near the high-J transitions of normal species were searched, because the low-J transitions have fairly broad linewidths and low intensities. Very low modulation voltages (*ca.* 10 V/cm) were used to prevent disturbances by the Stark lobes of the normal species and its strong excited states. The transitions of the ^{29}Si species were assigned on the basis of the intensity ratio to the lines of normal species, and the assignment was confirmed by the measurement of the intensity change between room and Dry Ice temperatures. Unfortunately, the line due to the ^{30}Si species could not be obtained, since the predicted positions were overlapped by the strong vibrational satellites. The observed transition frequencies are listed in Table 1. For the precise determination of the rotational constants, several transitions of normal species including low-J transitions were also measured. Since the observed peak positions differ from the hypothetical unsplit values because of the hyperfine structure due to the chlorine nuclei, the observed peak values were corrected to unsplit values[3] using the calculated frequency differences on the assumptions of $eqQ=-40$ MHz and $\angle$ClSiCl$=$108.6°. The rotational constant and the centrifugal distortion constant, D_J, were obtained by a least-squares fit of all the corrected transition frequencies in Table 1. The rotational constant of the ^{29}Si species listed in the table was determined from the high-J transitions, assuming the same D_J value.

The obtained rotational constants lead to the C–Si bond distance of 1.865 Å by the use of Kraitchman's equation, if the previously reported rotational constant of ^{13}C species[2] is included. This C–Si distance, which is close to that of methylsilane (1.867 Å), seemed too long considering that the substitution of the hydrogen atoms by the halogen atoms should cause a fairly large bong shortening;[4] in fact the C–Si distance in CH_3SiF_3 is 1.812 Å. Therefore, a reinvestigation of the spectrum of the ^{13}C species was undertaken. We tried to observe a few high-J transitions of the ^{13}C species, but we could not find them at the frequencies calculated from the B value reported in Ref. 2 except for the $J=9\leftarrow8$ transition, which is the only transition observed by Mitzlaff *et al.* Furthermore, the intensity measurements at room and Dry Ice temperatures showed that it was impossible that this transition belongs to the ground state line. Presumably it is to be ascribed to one of the excited vibrational states of the $^{35}Cl_2{}^{37}Cl$ species, since this region is near to its ground state transitions. We found several lines which should be ascribed to the spectrum of the ^{13}C species at slightly lower frequencies, as calculated from the reported value. The assignment was confirmed by a comparison of the intensities with those of the ^{29}Si species and by the change in the intensities between room and Dry Ice temperatures. The molecular structure, except for the methyl group, was determined by the substitution method, as Table 1 shows. The coordinates of the chlorine atoms were obtained by combining the A and B rotational constants of $^{35}Cl_2{}^{37}Cl$ species and the B rotational constants of the $^{35}Cl_3$ and $^{37}Cl_3$ species with a modification of Kraitchman's equation.[5] The obtained Si–C bond distance shows a clear bond shortening upon the substitution of chlorine atoms for hydrogen atoms attached to the silicon. The amount of the shortening is about a half of that by fluorine substitution, as has been estimated from the results for other molecules.[6]

Trichlorosilane. Mitzlaff *et al.* have also investigated the microwave spectrum of trichlorosilane. They have reported the eQV_{zz} to be $+12.8$ MHz, which was obtained from the measurement of the two strong lines in the $J=2\leftarrow1$ transition on the basis of the theory presented by Wolfe.[7] This theory, however, was found to be incorrect and was amended by Wolf *et al.* recently.[3] If we analyze the reported frequencies by means of the new theory, the eQV_{zz} of trichlorosilane becomes 8

TABLE 1. THE OBSERVED AND CALCULATED FREQUENCIES, ROTATIONAL PARAMETERS, AND MOLECULAR STRUCTURES OF TRICHLOROMETHYLSILANE AND TRICHLOROSILANE (MHz)

CH_3SiCl_3	$^{12}CH_3{}^{28}Si^{35}Cl_3$			$CH_3{}^{29}SiCl_3$	$^{13}CH_3SiCl_3$
J' — J	Obsd	Corr^a)	Obsd − Calcd		
4 — 3	14157.85	14158.32	0.01		
5 — 4	17697.54	17697.81	−0.03		
6 — 5	21237.05	21237.23	−0.09		
7 — 6	24776.70	24776.82	0.02		
8 — 7	28316.24	28316.33	0.11		
9 — 8	31855.67	b	0.09		31350.10
10 — 9	35394.13	b	0.03	35383.51	34832.78
11 — 10	38934.13	b	0.00		38315.98
12 — 11					41798.92
13 — 12	46012.36	b	−0.05		45281.90
14 — 13	49551.38	b	−0.04	49535.46	48764.91
B	1769.797			1769.228	1741.700
D_J	0.00026				
	r_s(Si-Cl) = 2.026 Å	∠Cl-Si-Cl = 108.6°			
	r_s(Si-C) = 1.848 Å	∠C-Si-Cl = 110.3°			

$SiHCl_3$	$HSi^{35}Cl_3$			$HSi^{37}Cl_3$	$H^{29}SiCl_3$
J' — J	Obsd	Corr^a)	Obsd − Calcd		
2 — 1	9888.07^c) 9890.19^c)	9889.89	−0.03		
3 — 2	14833.95	14834.84	0.02		
4 — 3	19779.23	19779.68	0.01		
5 — 4	24724.22	24724.49	0.06		
6 — 5	29668.86	29669.03	−0.06		
7 — 6	34613.57	34613.69	0.05	32845.83	34568.78
8 — 7	39558.00	b	−0.03	37537.65	39506.68
B	2472.468			2346.213	2469.279
D_J	0.00085				
eQq	−37.0				
	r_s(Si-H) = 1.464 Å	∠Cl-Si-Cl = 109.4°			
	r_s(Si-Cl) = 2.020 Å	∠H-Si-Cl = 109.5°			

a) The corrected frequencies considering the shift resulting from the nuclear quadrupole interaction. b) The correction was neglected. c) $K=1$ component.

MHz; this leads to −25 MHz of eQV_{aa}, by assuming ∠ClSiCl = 109.6°. This eQV_{aa} seemed too small compared with the eQq of −40 MHz in SiH_3Cl. Therefore, we reinvestigated the hyperfine structure of trichlorosilane.

The $J=2\leftarrow1$ transition was measured carefully and repeatedly, and two strong components were found at the values calculated from the high-J transitions and a reasonable eQV_{aa} value. We did not find strong lines at the frequencies reported by Mitzlaff *et al.* From these two components, the eQV_{zz} is determined to be 12 MHz, which leads to an eQV_{aa} value of −37 MHz. This value is quite reasonable as the quadrupole coupling constant of the chlorine atom attached to silicon. The rotational constants obtained by Mitzlaff *et al.* were also refined using the quadrupole coupling constant newly determined by the method used for the analysis of methyltrichlorosilane; they were determined to be as listed in the table. The molecular structure was also recalculated with these rotational constants by means of the substitution method. However, the change in the molecular structure is small, since the changes in the rotational constants are very small.

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