Microwave Spectra and Barrier to Internal Rotation in Cyclopropylmethylsilane

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Rotational spectra for 3 silicon isotopologues (^{28}Si, ^{29}Si, ^{30}Si) of cyclopropylmethylsilane (c-$C_3H_5SiH_2CH_3$) have been observed in natural abundance using Fourier-transform microwave spectroscopy, and the dipole moment of the most abundant (^{28}Si) isotopologue has been determined using the Stark effect. The observed rotational constants ($A = 8800.5997(9)$ MHz; $B = 2238.6011(3)$ MHz; $C = 2001.0579(3)$ MHz) and dipole moment components ($\mu_a = 0.195(2)$ D, $\mu_b = 0.674(11)$ D, $\mu_c = 0.362(19)$ D, $\mu_{\text{total}} = 0.790(13)$ D) for the ^{28}Si species are consistent with ab initio predictions (MP2/6-311+G(d)) for a gauche conformation about the Si-cyclopropyl bond. All of the observed transitions were split into doublets due to internal rotation of the methyl group, allowing a determination of the V_3 barrier to internal rotation of 6.671(9) kJ mol^{-1} for the most abundant isotopologue. This barrier will be compared to those for other Si-CH_3 containing compounds and will be related to a partial structure determination from the available microwave and ab initio data.

I. Introduction

The silicon analogues of alkanes provide interesting comparisons of molecular properties, while also helping to elucidate the variation in bond length, bond angles, and barriers to internal rotation observed upon substituting a silicon atom in place of a carbon atom. In cyclopropylmethylsilane (CMS), it is possible that the distortions caused by the strained cyclopropyl group will lead to differences in the Si−C distances and possibly C−Si−C angles compared to other compounds containing silicon atoms. Recent studies on ethylsilane,[1] propylsilane,[1] and diethylsilane[2] give C−Si distances ranging from 1.864 to 1.870 Å, with H−Si−C or C−Si−C angles between 109.6 and 111.2°. Because the cyclopropyl group will significantly distort the bonding and hybridization around atom C_2 in CMS (the cyclopropyl carbon, part a of Figure 1 shows atom numbering), it is likely that the Si−C_2 distance will be quite different than the observed parameters in the previously studied ethyl- and propylsilanes, as well as differing from the Si−CH_3 distance.

From a spectroscopic standpoint, CMS is interesting due to the presence of a methyl group attached to the silicon atom (part a of Figure 1). This group is likely to undergo a low barrier internal rotation. Additionally, a rotation about the bond between the cyclopropyl group and the silicon atom leads to the possibility of multiple conformers. Three likely structures of CMS were considered, as shown in part b of Figure 1. Of these, the gauche conformer is expected to be the lowest in energy because the methyl group is aligned between one side of the cyclopropyl ring and a hydrogen atom, leading to a less sterically hindered arrangement. The cis conformer (second-lowest energy) could also have some population in the supersonic expansion, because the methyl group is oriented between the two CH_2 units of the cyclopropyl group, although some degree of steric hindrance could raise the energy of this structure relative to the gauche configuration. Finally, the trans conformer is expected to be relatively high in energy due to its eclipsed orientation and, in fact, recent ab initio calculations revealed that this conformer is a transition state rather than a stable minimum.[3] There is the possibility of one other conformer in which the methyl group eclipses one side of the cyclopropyl group, but the bulkiness of the eclipsing groups is likely to make this structure significantly higher in energy than any of the other three; thus, it was not considered as a feasible conformation in the molecular beam. The supersonic molecular expansion lowers the effective temperature of the gas, making it likely that only the lowest-energy conformer will be significantly populated. A recent low-temperature infrared and Raman study by Durig, et al.[3] led to the observation of the two lowest-energy conformers of CMS in liquid xenon solution, and the enthalpy of isomerization from the gauche to the cis conformer was determined to be 1.17(16) kJ mol^{-1} under these conditions and 1.21(44) kJ mol^{-1} in the pure liquid; however, the IR study was not able to determine the barrier to rotation of the methyl group.

The microwave spectra of a variety of silicon-containing compounds have been measured over the last several decades.[1,2,4−19] Many of these compounds contain one or more halogen atoms,[10−13,17−19] in contrast to the purely hydrocarbon substituents of CMS. Many of the previously studied silicon compounds also contain one or more methyl groups attached to the silicon atom, making it possible to compare internal rotation barriers quite extensively.[5−8,10,12,17−19] It appears that the barrier

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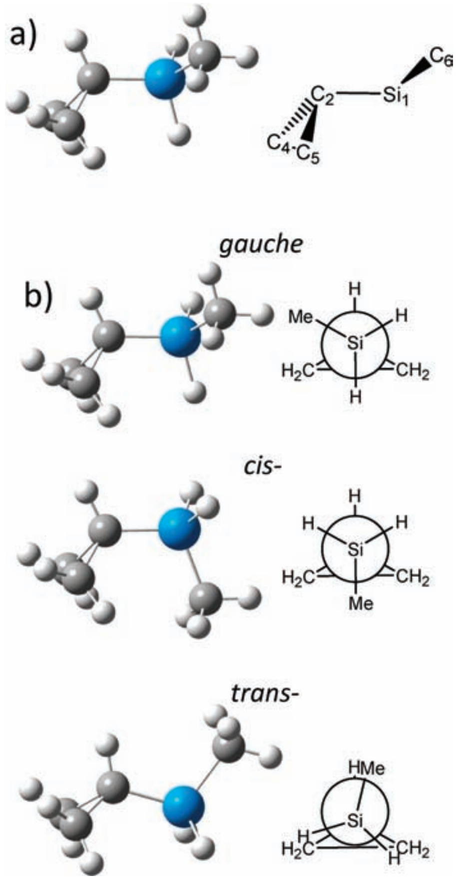

Figure 1. (a) Ball and stick structure of the most stable gauche conformer of cyclopropylmethyl silane (CMS), and a heavy-atom structure showing the atom numbering. (b) Newman projections of the two stable conformers (gauche, cis) and the trans transition state of CMS. The silicon atom is in the front, looking down the Si−C(cyclopropyl) bond.

to internal rotation about the Si−C bond (∼6.5 kJ/mol) is typically lower than the average barrier about a C−C bond (∼12 kJ/mol).[20] It will be of interest both to determine whether the internal rotation barrier in CMS is equally low, as there is a possibility of steric hindrance from the nearby cyclopropyl group, and to investigate the differences between barriers in halogenated and nonhalogenated compounds. The availability of data from Fourier-transform microwave (FTMW) spectroscopy will also allow a determination of structural details that may help in our understanding of differences in both the methyl internal rotation barrier and conformer stability when compared with similar species.

In the current work, we report an investigation of the FTMW spectrum of CMS. This has allowed a determination of the dipole moment, rotational constants, and barrier to methyl group internal rotation for the lowest-energy conformer of the compound and a comparison with ab initio predictions. A complementary investigation of CMS using liquid- and solid-phase infrared and Raman spectroscopy has been published separately.[3] That paper reports a fitted structure based on the rotational constants determined in the present microwave study combined with their ab initio results (referred to as an A&M [ab initio and microwave] structure[21]). In the present study, the fitting of the internal rotation doublets from the methyl top in CMS has allowed us to determine several structural parameters directly from the experimental data, and these will be compared with the ab initio and A&M structures and with a partial inertial fit structure.

II. Experimental Section

A sample of CMS was synthesized and purified as described in ref 3. A sample consisting of roughly 1% CMS in 2.5 bar He/Ne (82.5% Ne:17.5% He, BOC Gases) was prepared by condensing a small amount of vapor into a glass sample bulb using standard gas handling techniques. The FTMW spectrometer at Eastern Illinois University (which has been described in more detail previously[22]) follows the Balle-Flygare design,[23] incorporating hardware and software developments from the University of Kiel.[24] The spectra of three isotopologues of CMS, corresponding to the three naturally occurring silicon isotopes (^{28}Si = 92.23%, ^{29}Si = 4.68%, ^{30}Si = 3.09%), were assigned in natural abundance. The strongest transitions had signal-to-noise (*S*/*N*) ratios of 40−45 in 100 gas pulses, whereas more typical *S*/*N* ratios of about 10 (after 100−200 nozzle shots) were observed for transitions belonging to the ^{28}Si species. A perpendicular nozzle configuration is used for these experiments, leading to broader lines (full-width at half-maximum ∼30 kHz) than typically observed with a coaxial configuration. Transitions at higher frequencies show a small but resolvable Doppler doubling, and when this was apparent the average frequency was used in the fit.

To measure the dipole moment of CMS, a voltage of up to ± 5 kV (corresponding to a maximum field of ∼320 V/cm) was applied across a pair of parallel steel mesh plates separated by about 30 cm. The microwave antenna was aligned parallel to the direction of the electric field so that only $\Delta M = 0$ transitions were observed, and the field was calibrated by measurement of the $J = 1 \leftarrow 0$ transition of OCS, assuming a dipole moment of 0.71519(3) D.[25]

The three conformers of CMS were optimized at the MP2/6-311+G(d) level using *Gaussian 03*.[26] These calculations supplement the much more extensive ab initio study performed in ref 3.

III. Results

A. Spectra. The rotational spectra of the ^{28}Si, ^{29}Si, and ^{30}Si isotopologues of CMS were recorded in the range 5−16 GHz. All observed lines were split by ∼15−350 kHz into doublets that were assigned to *A* and *E* state transitions, arising from internal rotation of the methyl group. Six *a*-type, 11 *b*-type, and 5 *c*-type transitions were assigned for the normal isotopologue, with smaller data sets for the ^{29}Si and ^{30}Si species as a result of their lower natural abundances. The frequencies of the assigned transitions for all three isotopologues are given in Table 1. The data were fitted to a Watson *A*-reduction Hamiltonian in the I^r representation,[27] with additional terms included to account for internal rotation. The IAM model[28] as implemented in the *XIAM* program[29] was used for the fitting procedure. The resulting spectroscopic constants are listed in Table 2.

In the initial fits, in addition to the usual semirigid Hamiltonian terms (rotational and fourth-order distortion constants), an attempt was made to fit the V_3 barrier, the angle δ (between the internal rotation axis of the methyl top and the *a* inertial axis of the molecule), and F_0 (the rotational constant of the methyl top). The angle, ε, between the *b* axis and the projection of the internal rotor axis in the *bc* plane was fixed to 0° because attempts to fit it did not converge and ab initio results predicted that the methyl group lies very close to the *bc* plane. This is the same combination of parameters that was successfully determined recently for the analogous compound cyclopropylmethylgermane (CMG);[30] however, for CMS, V_3 and F_0 were strongly correlated in the least-squares fitting routine, and the resulting value of F_0 of about 163 GHz was far outside the

TABLE 1: Observed Frequencies for the Measured Rotational Transitions of the ^{28}Si, ^{29}Si, and ^{30}Si Isotopologues of Cyclopropylmethylsilane (CMS)

			^{28}Si-CMS		^{29}Si-CMS		^{30}Si-CMS	
$J'_{Ka'Kc'}$	$J''_{Ka''Kc''}$	state	ν/MHz	$\Delta\nu$/kHz[a]	ν/MHz	$\Delta\nu$/kHz[a]	ν/MHz	$\Delta\nu$/kHz[a]
3_{13}	3_{03}	*A*	5996.1848	−1.9				
		E	5996.0079	5.4				
2_{12}	2_{02}	*A*	6331.0159	2.9	6287.3271	5.7	6245.7222	3.9
		E	6330.8096	3.9	6287.1132	−1.1	6245.5252	6.2
3_{03}	2_{12}	*A*	6362.6011	1.3				
		E	6362.7750	3.1				
1_{11}	1_{01}	*A*	6562.1664	−0.4	6519.2102	2.3	6478.2796	−4.1
		E	6561.9202	−2.6	6518.9617	−2.1	6478.0394	−10.1
1_{10}	1_{01}	*A*	6799.6832	−3.5	6757.5481	3.2	6717.3806	0.3
		E	6799.5026	−3.0	6757.3630	−1.2	6717.2041	−1.0
2_{11}	2_{02}	*A*	7043.5617	−0.8	7002.3264	4.1	6962.9973	−0.7
		E	7043.3420	−2.4	7002.1013	−3.1	6962.7863	−1.1
3_{12}	3_{03}	*A*	7421.1534	3.7	7381.4144	−3.6	7343.4998	−3.1
		E	7420.9064	0.0	7381.1721	−2.6	7343.2728	4.8
4_{13}	4_{04}	*A*	7946.2458	−4.5				
		E	7945.9762	−1.4				
2_{12}	1_{11}	*A*	8241.8191	−2.0				
		E	8241.8359	2.2				
2_{02}	1_{01}	*A*	8472.9753	0.4				
		E	8472.9508	0.1				
5_{14}	5_{05}	*A*	8636.4641	3.8				
		E	8636.1514	1.2				
2_{11}	1_{10}	*A*	8716.8497	−1.0				
		E	8716.7881	−1.4				
6_{15}	6_{06}	*A*	9512.0002	−1.2				
		E	9511.6439	−0.3				
1_{11}	0_{00}	*A*	10801.8306	0.1	10742.4931	−1.3	10685.6938	0.2
		E	10801.5737	−0.5	10742.2421	4.1	10685.4529	5.6
4_{04}	3_{13}	*A*	10899.2217	−1.1				
		E	10899.3632	1.0				
1_{10}	0_{00}	*A*	11039.3465	−3.8	10980.8227	−8.7	10924.7923	2.1
		E	11039.1633	6.3	10980.6413	2.9	10924.6050	2.0
3_{13}	2_{12}	*A*	12358.7846	−1.9				
		E	12358.7699	−4.4				
3_{03}	2_{02}	*A*	12693.6155	2.7				
		E	12693.5750	−2.6				
3_{12}	2_{11}	*A*	13071.1979	−2.1				
		E	13071.1410	1.4				
2_{12}	1_{01}	*A*	14803.9882	0.3	14727.4523	−5.3	14654.0173	−3.1
		E	14803.7550	−1.5	14727.2227	−3.5	14653.7963	−1.3
2_{11}	1_{01}	*A*	15516.5400	2.6	15442.4623	3.9	15371.3036	3.5
		E	15516.2972	2.1	15442.2226	6.4	15371.0619	−4.1
5_{05}	4_{14}	*A*	15500.6999	−0.9				
		E	15500.8104	1.4				

[a] $\Delta\nu = \nu_{\mathrm{obs}} - \nu_{\mathrm{calcd}}$.

expected range for methyl groups (∼157−159 GHz, as discussed in the *XIAM* documentation).[29,31] To break the correlation, in the final fits for CMS the value of F_0 was fixed to the average value of 159.3 GHz that was determined for the five isotopologues of CMG (corresponding to a moment of inertia of the top, I_α, of 3.17 u Å^2),[30] as ab initio calculations predict less than 1% difference in the I_α values for the two species. The resulting fitted values of V_3 and δ are shown in the first column of Table 2. Although the angle δ is not significantly different from the fit in which F_0 was varied, the V_3 barrier is about 0.15 kJ mol^{-1} (about 2% of its value) lower than it was when F_0 was allowed to vary.

In an effort to get a better idea of the values of both δ and ε, a second series of fits (with I_α again fixed to 3.17 u Å^2) was performed in which ε was systematically varied through a range of (fixed) values from 0−8°. It was found that the lowest standard deviation for the fit (by only 0.001 kHz) was obtained with a value of $\varepsilon = 7°$. This is within 5° of the ab initio value (2.7° at the MP2/6-311+G(d) level, assuming that the top axis coincides with the C−Si bond) and also leads to slightly better agreement between the other structural parameters and the predicted values. This final best fit of the spectroscopic parameters is given, along with the corresponding fits for the ^{29}Si and ^{30}Si species, in the second through fourth columns of Table 2. The ab initio parameters for the gauche structure have also been included in Table 2 for comparison.

B. Structure. Because only three isotopologues were observed for CMS, there are not enough experimental moments of inertia to determine the 39 structural parameters of the molecule; however, because the rotational constants are in good agreement with the ab initio predictions, it can be assumed that the theoretical structural parameters provide a reasonable estimate of the true structure of the molecule. A partial least-squares fit of the observed moments of inertia to sets of one to five structural parameters directly involving the silicon atom (because it was the isotopically substituted atom) while keeping the other parameters fixed at the ab initio values has also been performed. Average values of the inertial fit parameters (from

TABLE 2: Fitted Spectroscopic and Internal Rotation Constants for the Three Assigned Cyclopropylmethylsilane Isotopologues; Ab Initio Parameters for the Gauche Conformer Are also Included for Comparison

	^{28}Si-CMS		^{29}Si-CMS	^{30}Si-CMS	
	ε [a] = 0°	ε = 7° (Best Fit)	ε = 7°	ε = 7°	ab initio (gauche, ^{28}Si)[b]
A/MHz	8800.5997(9)	8800.5997(9)	8749.8609(21)	8701.3834(21)	8726
B/MHz	2238.6012(3)	2238.6011(3)	2230.8209(9)	2223.2625(9)	2222
C/MHz	2001.0578(3)	2001.0579(3)	1992.4609(7)	1984.1429(7)	1983
Δ_J/kHz	0.872(9)	0.872(9)	0.872 [c]	0.872 [c]	
Δ_{JK}/kHz	−7.39(11)	−7.39(11)	−7.39 [c]	−7.39 [c]	
δ_J/kHz	0.212(3)	0.212(3)	0.212 [c]	0.212 [c]	
P_{aa}/u Å^2 [d]	210.44351(4)	210.44351(4)	211.21554(10)	211.97141(19)	212.2
P_{bb}/u Å^2 [d]	42.11242(4)	42.11241(4)	42.43010(10)	42.73757(19)	42.66
P_{cc}/u Å^2 [d]	15.31310(4)	15.31311(4)	15.32842(10)	15.34274(19)	15.25
V_3/kJ mol^{-1}	6.684(9)	6.671(9)	6.66(1)	6.68(1)	5.8 [e]
I_α/u Å^2 [f]	3.17 [g]	3.17 [g]	3.17 [g]	3.17 [g]	3.14
δ/° [f]	42.7(2)	43.0(2)	43.0 [c]	43.0 [c]	43.6
s.d./kHz [h]	2.9	2.9	4.8	4.7	

[a] ε is the angle between the b axis and the projection of the internal rotor axis in the bc plane. [b] Ab initio calculations at the MP2/6-311+G(d) level. [c] These parameters were fixed at the values from the ^{28}Si isotopologue. [d] Planar moments are derived from the fitted rotational constants. [e] A crude estimate of the barrier is obtained by taking the difference between the ab initio energies of the gauche structure with staggered and eclipsed methyl group orientations. [f] I_α is the moment of inertia of the top. δ is the angle between the internal rotation axis and the a principal axis of the molecule. [g] Fixed at the average value determined for the five assigned isotopologues of cyclopropylmethyl germane.[30] [h] s.d. = standard deviation of the fit.

TABLE 3: Results of Ab Initio Calculations (MP2/6-311+G(d) Level) and Spectroscopic and Inertial Fits of Various Combinations of Structural Parameters of CMS and Comparison with Derived Structural Parameters from a Combination of Microwave and Ab Initio Data (A&M Structure, Explained in Text and Ref 3)

	ab initio	spectroscopic fit[a]	inertial fit[b]	A&M structure[c]
$R(\text{Si}_1-\text{C}_6)$/Å	1.878		1.86(3)	1.871(5)
$R(\text{Si}_1-\text{C}_2)$/Å	1.861		1.85(3)	1.852(5)
$R(\text{C}_2-\text{C}_4)$/Å	1.524			1.518(3)
$R(\text{C}_2-\text{C}_5)$/Å	1.523			1.519(3)
$R(\text{C}_4-\text{C}_5)$/Å	1.502			1.500(3)
$\theta(\text{C}_6-\text{Si}_1-\text{C}_2)$/°	111.3		111.3(7)	111.5(5)
$\theta(\text{Si}_1-\text{C}_2-\text{C}_4)$/°	119.6		119.7(7)	119.9(5)
$\theta(\text{C}_2-\text{C}_4-\text{C}_5)$/°	60.4			60.5(5)
$\phi(\text{C}_6-\text{Si}_1-\text{C}_2-\text{C}_4)$/°	−152.4		−153.2(8)	−152.9(5)
$\phi(\text{Si}_1-\text{C}_2-\text{C}_4-\text{C}_5)$/°	108.4			
δ/°	43.6 [d]	43.0(2)		
ε/°	2.7 [d]	7		

[a] Only δ and ε can be determined directly from the fit of the A and E state transitions using the *XIAM* program.[29] ε was determined indirectly, as discussed in the text. [b] Average parameters and standard deviations from fits of up to five structural parameters involving the Si atom to the nine moments of inertia derived from the experiment. [c] Ref 3. [d] Assumes that the internal rotation axis of the top coincides with the Si−C bond of CMS.

TABLE 4: Ab Initio (MP2/6-311+G(d)) Rotational Constants and Dipole Moment Components for the Gauche, Cis, and Trans Conformers of Cyclopropylmethylsilane

	gauche	cis	trans	experiment
relative energy/cm^{-1}	0	89	629	
A/MHz	8726	6625	9728	8800.5997(9)
B/MHz	2222	2612	1987	2238.6011(3)
C/MHz	1983	2287	1962	2001.0579(3)
P_{aa}/u Å^2	212.2	169.1	230.0	210.4
P_{bb}/u Å^2	42.66	51.89	27.60	42.11
P_{cc}/u Å^2	15.25	24.39	24.36	15.31
μ_a/D	0.22	0.53	0.13	0.195(2)
μ_b/D	0.64	0.52	0.76	0.674(11)
μ_c/D	0.35	0.00	0.00	0.362(19)
μ_{tot}/D	0.77	0.74	0.77	0.790(13)

TABLE 5: Kraitchman and MP2/6-311+G(d) Principal Axis Coordinates (in Angstroms) for the Silicon Atom in CMS

	a	b	c
Kraitchman Results:[a]			
^{29}Si	−0.8831(17)	0.5682(26)	0.1255(120)
^{30}Si	−0.8831(17)	0.5682(26)	0.1251(120)
Ab Initio Results:			
gauche	−0.8923	0.5771	0.1283
cis	1.0440	−0.6202	0.0000
trans	−0.8894	0.5314	0.0000

[a] The uncertainties in the Kraitchman coordinates are the Costain errors as described in ref 34. Signs for the Kraitchman coordinates are assumed based on the ab initio results.

the 12 fits performed) are summarized in Table 3. The lack of precision in these values reflects the fact that all of the isotopic substitutions involved only one atom within the molecule. Although quite approximate, the inertial fit data are in reasonable agreement with both the ab initio results presented in the current article and the A&M structure derived by Durig, et al.[3]

A limited amount of additional structural information is available from the internal rotation fit (performed using *XIAM*[29]). The spectroscopic fitting procedure (section III.A, above) leads to an angle (δ) between the internal rotor axis and the a principal axis of 43.0(2)°, within 0.6° of the ab initio prediction for the gauche structure. The derived planar moments ($P_{aa} = (1/2)(I_{bb} + I_{cc} - I_{aa})$ and permutations) for the experimental and gauche ab initio structures are also in good agreement for this conformer (Tables 2 and 4). The P_{aa} and P_{bb} values for the ^{29}Si and ^{30}Si isotopologues are slightly larger than for the normal species while P_{cc} hardly changes, indicating that the silicon atom lies near the center of mass and close to the ab plane of the molecule. These results are confirmed by the substitution coordinates (discussed below).

The isotopic substitution of the silicon atom allows determination of its principal axis coordinates directly through the use of Kraitchman's equations.[32] These calculations were performed using Kisiel's *KRA* program,[33] with the resulting coordinates and uncertainties[34] for both the ^{29}Si and ^{30}Si species given in Table 5 (with signs taken from the ab initio structure), where they are also compared with the ab initio coordinates for the silicon atom. Whereas the a coordinate of the silicon atom is

TABLE 6: Dipole Moment Components and Observed and Least-Squares Fitted Values of the Stark Coefficients, $\Delta\nu/E^2$, in Units of 10^{-6} MHz V^{-2} cm^2 for Cyclopropylmethylsilane

			Stark Coefficients			Percent Error
J'_{KaKc}	J''_{KaKc}	$\|M\|$	observed	calculated	obs − calcd	
1_{11}	0_{00}	0	3.371	3.377	−0.006	−0.2
1_{10}	0_{00}	0	3.745	3.791	−0.047	−1.3
1_{10}	1_{01}	1	19.72	19.66	0.066	0.3
1_{11}	1_{01}	1	−5.675	−5.737	0.062	−1.1
2_{12}	1_{01}	1	6.169	6.222	−0.053	−0.9
2_{11}	1_{01}	1	7.995	8.047	−0.052	−0.7
			Dipole moment components:			
			μ_a/D	0.195(2)		
			μ_b/D	0.674(11)		
			μ_c/D	0.362(19)		
			μ_{total}/D	0.790(13)		

TABLE 7: Comparison of Methyl Group Barriers to Rotation in a Selection of Silicon and Germanium Compounds

	V_3/kJ mol^{-1}		
compound	X = Si	X = Ge	reference
$MeXH_2(C_3H_5)$	6.671(9)	4.736(6)	this work, 30
$MeXH_3$	6.67(20)	5.18(11)	5, 36
$MeXH_2F$	6.52(13)	3.94(8)	17, 37
Me_2XH_2	6.910(42)	4.94(17)	8, 38
Me_3XCl	6.901(11)	4.45440(3)	18, 39
Me_3XBr		4.783(12)	40
Me_3XI	7.4151(36)		19

similar to both the gauche and trans ab initio structures, the *b* and *c* coordinates only agree closely with the gauche conformer. This serves as further confirmation that the observed structure is gauche. In addition, the nonzero values for the silicon coordinates can be taken as an indication that the Si−C bond (and therefore the methyl group) does not lie in the *bc* inertial plane. This is consistent with the apparent preference for a slightly nonzero value for the angle ε discussed in section III.A above.

C. Dipole Moment. The dipole moment of CMS was determined by measuring the Stark effects of six *M* components from six *A*-state rotational transitions. The maximum observed shift of an *M* component was ~880 kHz, with no total shift of less than ~300 kHz included in the fit. The Stark coefficients obtained by plotting $\Delta\nu$ versus E^2 for each component were least-squares fitted to those predicted from the rotational constants in Table 2.[35] All of the differences between observed and calculated Stark coefficients in the resulting fit were less than ~1.5% (Table 6). This procedure gave dipole moment components of $\mu_a = 0.195(2)$ D, $\mu_b = 0.674(11)$ D, $\mu_c = 0.362(19)$ D, and $\mu_{total} = 0.790(13)$ D. These are in reasonable agreement with the ab initio prediction (Table 4).

IV. Discussion

A. Conformers and Structure. Ab initio calculations (performed using *Gaussian 03*[26] at the MP2/6-311+G(d) level) confirm the intuitive ideas, discussed in the Introduction, about the relative energies of the three conformers. The results of these calculations are summarized in Table 4 and, for this study, were used primarily as confirmation of assignment of the correct conformer and as a tool for predicting the rotational constants and dipole moment of the conformers prior to searching for the spectra. A much more extensive computational study of CMS has been performed concurrently with the infrared and Raman study and is reported elsewhere.[3]

Comparison of our ab initio rotational constants and dipole moment components with the experimental values (Tables 2 and 4) shows unambiguously that the observed conformer is the gauche structure. Both the cis and trans conformations have C_s symmetry, and would therefore be expected to have $\mu_c = 0$, whereas the experimentally observed structure has a nonzero μ_c dipole moment component (Table 6). All three rotational constants agree to within 1% with the ab initio values for the gauche structure, whereas the discrepancies for the cis and trans structures are much larger.

The structural parameters for CMS may be compared with those of ethylsilane,[1] propylsilane,[1] and diethylsilane[2] to get an idea of how the presence of both the cyclopropyl group and the silicon atom affect the structure in comparison with other silicon-containing compounds. At 1.86(3) and 1.85(3) Å (inertial fit), the Si−C bonds in CMS are approximately the same length as the bonds in ethylsilane,[1] *trans*-propylsilane,[1] and diethylsilane[2] (which range from 1.864 to 1.870 Å). The 0.01 Å difference between the two Si−C distances within CMS is significant, however, with the ab initio and A&M structures giving even larger differences of 0.017 and 0.019 Å,[3] respectively. In all cases, the shorter distance is that between the cyclopropyl carbon (C_2) and the silicon atom. This shortening of the bond to the cyclopropyl group might be further explained by a natural bond orbital (NBO) analysis; however, such an investigation is beyond the scope of the current study.

B. Barrier to Rotation. Our best value for the barrier to internal rotation of the ^{28}Si isotopologue is 6.671(9) kJ mol^{-1}. This is in good agreement with the barriers derived for Si−CH_3 groups in other compounds, as can be seen from the representative species in Table 7 and the chart in Figure 2,[5,8,17−19] where analogous germanium species have been included for comparison.[19,30,36−40] It is interesting that the barrier for CMS is essentially identical to that of methylsilane, whereas the barrier for methylgermane is significantly higher than that of cyclopropylmethylgermane, although this could be partly due to the large uncertainties of both the methylsilane and methylgermane barriers. One conclusion that can be drawn from these observations is that the cyclopropyl group does not lead to an increased barrier, which might have been expected based solely on steric considerations; however, for the silicon compounds, it appears that the barriers do increase with the addition of more methyl groups to the molecule. In addition, it appears that the presence of a fluorine atom bound to silicon or germanium lowers the barrier to rotation in both $MeSiH_2F$ and $MeGeH_2F$.

It is also notable that the barriers in the silicon compounds are consistently about 2 kJ mol^{-1} higher than those in the corresponding germanium species. One possible explanation for the higher barriers in the silicon compounds is the smaller size

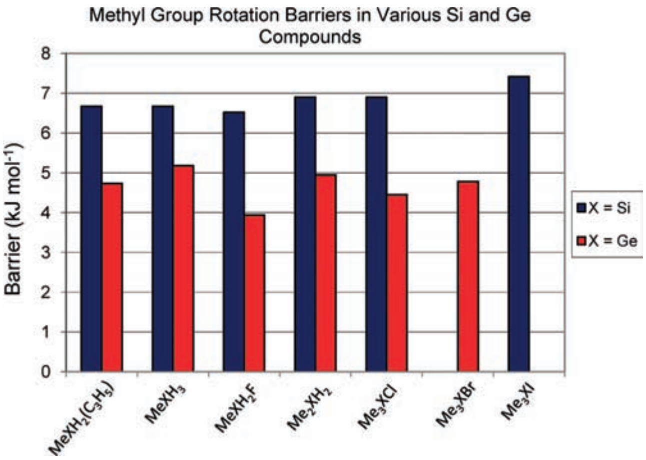

Figure 2. Comparison of barrier to internal rotation in a series of silicon and germanium containing compounds. See Table 7 for numerical data and references.

of silicon atoms (r = 1.17 Å, covalent radius) compared to germanium (r = 1.22 Å).[41] If this is the case, then the analogous carbon compounds (r_{sp3} = 0.772 Å) would be expected to have even larger barriers to internal rotation. Assuming that the difference is roughly proportional to the change in bond length, the C−Me barriers should be significantly larger than the Si−Me barriers, on the basis of the difference between Si−Me and Ge−Me. The barriers to internal rotation in ethane and several other hydrocarbons are roughly 12 kJ mol^{-1}, [20] confirming this trend. Microwave studies of ethyl cyclopropane and cyclopropylmethylgermane would help to probe this connection more directly. A microwave study of cyclopropylmethylgermane has been performed (giving a C−Me barrier of 4.729(6) kJ mol^{-1}) and will be published separately;[30] however, few if any hydrocarbon compounds directly analogous to those listed in Table 7 have been studied due to their generally low polarities. The dipole moment of ethyl cyclopropane is predicted to be ∼0.08 D,[42] near the limit of detection for many FTMW spectrometers. A molecular mechanics study by Ouellette[43] does offer some further confirmation that the barriers to internal rotation for methyl groups bound to group 14 elements decrease as the atomic radius of the atom increases.

V. Conclusions

The spectra of the three silicon isotopologues of cyclopropylmethylsilane are in good agreement with ab initio predictions at the MP2/6-311+G(d) level. The gauche species was the only one of the three possible conformers of CMS observed in the low-temperature supersonic expansion. Although the energy of the cis conformer is low enough that it could also be present, no possible candidates for rotational transitions belonging to this species have been observed. The methyl group rotates with a barrier of about 6.671(9) kJ mol^{-1}, and this causes splitting of the spectrum into closely spaced A and E states. r_s substitution coordinates for the silicon atom derived from the ^{29}Si and ^{30}Si substitutions show reasonable agreement with the ab initio calculations. In addition, a structure derived by Durig, et al.[3] using our rotational constants in combination with their (more extensive) ab initio study is in reasonable agreement with the structural data obtained in the present work, both from the spectroscopic fitting procedure and from a least-squares fit of a few structural parameters to the available isotopic data.

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